**US Army Corps
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2,4,6-Trinitrotoluene (TNT) Transformation/Sorption in Thin-Disk Soil Columns Under Anaerobic Conditions

*by   Trudy J. Olin, Tommy E. Myers, WES
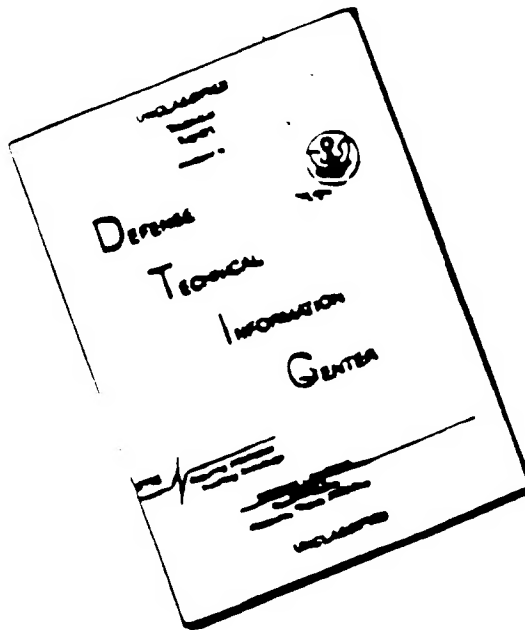Dan M. Townsend, Louisiana State University*

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2,4,6-Trinitrotoluene (TNT) Transformation/Sorption in Thin-Disk Soil Columns Under Anaerobic Conditions

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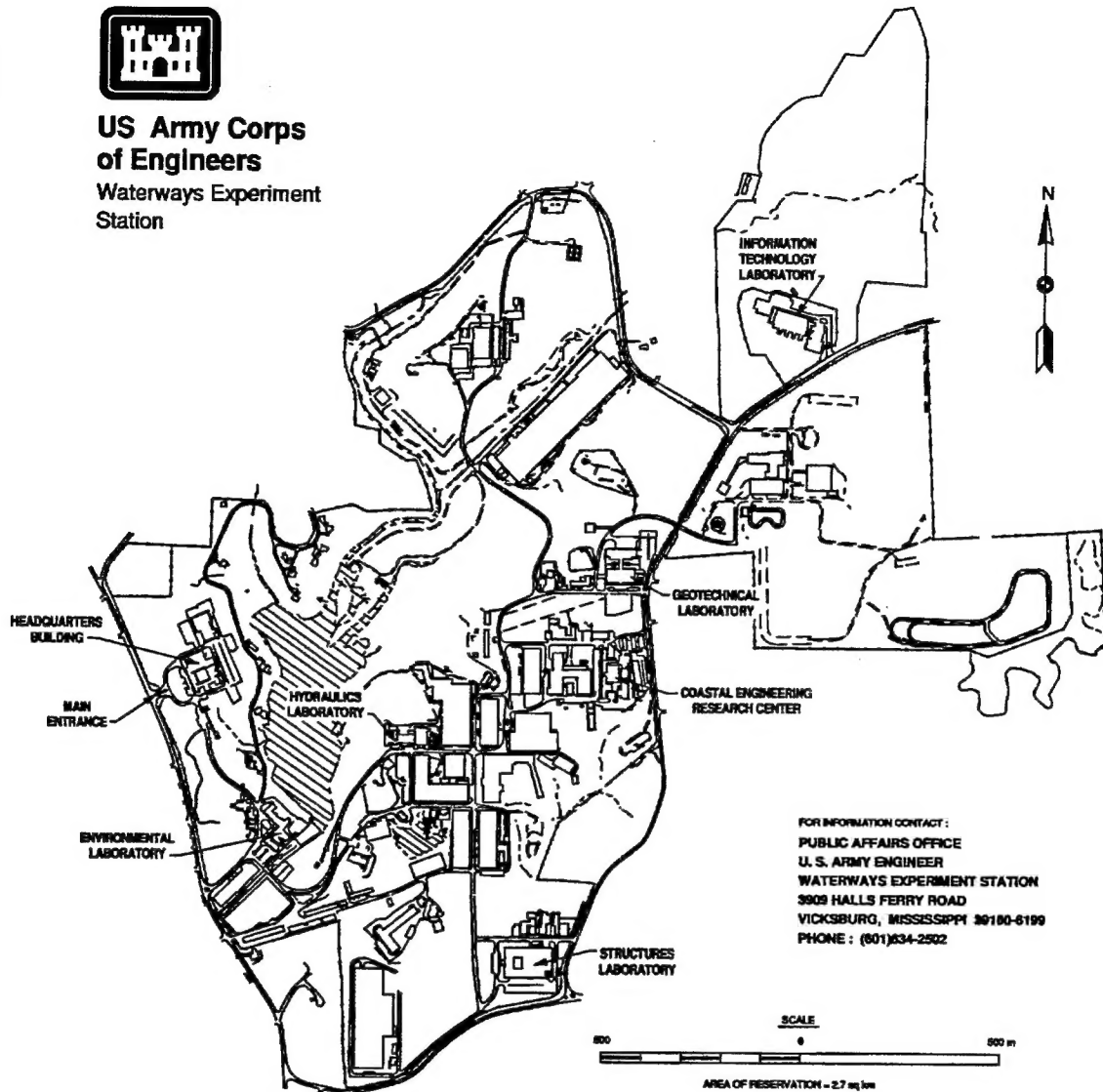Final report

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Preface

The work reported herein was conducted by the Environmental Laboratory (EL) of the U.S. Army Engineer Waterways Experiment Station (WES) for Headquarters, U.S. Army Corps of Engineers (HQUSACE). Funding was provided by the HQUSACE Installation Restoration Research Program (IRRP), Work Unit AF25-GW-003. Dr. Clem Myer was the IRRP Coordinator at the Directorate of Research and Development, HQUSACE. Technical Monitors were Messrs. George O'Rourke and David Becker. The IRRP Program Manager was Dr. M. John Cullinane, Jr.

This report was prepared by Ms. Trudy J. Olin, Environmental Resources Engineering Branch (EREB), Environmental Engineering Division (EED), EL; Mr. Tommy E. Myers, Environmental Restoration Branch (ERB), EED; and Mr. Dan M. Townsend, Contract-Graduate Student, Louisiana State University, Baton Rouge, LA. Dr. Paul R. Schroeder, Special Projects Branch, EED, and Mr. Christian J. McGrath, Contaminant and Water Quality Modeling Branch, Environmental Processes and Effects Division, EL, were technical reviewers for this report. Chemical analysis was performed by Ms. Karen Myers, Environmental Chemistry Branch, EED. Mr. Andrew J. Green, AScI Corporation, assisted with soil column operation and sampling.

The work was conducted under the direct supervision of Mr. Thomas R. Patin, Chief, EREB, and Mr. Daniel E. Averett, Chief, ERB, and under the general supervision of Mr. Norman R. Francingues, Jr., Chief, EED, and Dr. John W. Keeley, Director, EL.

At the time of publication of this report, Dr. Robert W. Whalin was Director of WES. Commander was COL Bruce K. Howard, EN.

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1   Introduction

Background

The sorption and transformation behavior of 2,4,6-trinitrotoluene (TNT) is important to modeling and remediation efforts at military installations where subsurface contamination exists in connection with munitions production. Processes potentially affecting the fate and transport of TNT in soils and groundwater include biotic and abiotic transformation, sorption, advection, hydrodynamic dispersion, dissolution, diffusion, and facilitated transport by organic and inorganic colloids (McGrath 1995). TNT breakthrough curves may provide indications of the type of processes occurring. The transformation rate of TNT is of particular interest in determining the long-term risk associated with TNT contamination in a soil.

Previous Studies

Equilibrium and transport models

Large length-to-diameter soil columns often are used in laboratory studies of contaminant transport in soils. When modeled, these columns are usually modeled with advection-dispersion models that account for mixing along the column length. The classical form of the advection-dispersion equation for reactive solutes in soil solution is (Selim 1992)

$$\theta\frac{\partial C}{\partial t} + \rho\frac{\partial S}{\partial t} = \theta D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial Z} - \sum_i \Psi_i \tag{1}$$

where

Θ = soil water content, cm^3/cm^3

C = solute concentration in solution, $\mu g/mL$

t = time, hr

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ρ = soil bulk density, g/cm^3

S = solute concentration associated with solid phase of soil, μg/g soil

D = hydrodynamic dispersion coefficient, cm^2/hr

z = depth, cm

v = Darcy's water flux density, cm/hr

Ψ_i = rates of solute removal (or supply) from soil solution, μg/cm^3·hr, and not included in S

The advection/dispersion equation is general in form and does not specify the processes occurring in sorption and transformation of TNT ($\partial S/\partial t$ and $\Sigma_i \Psi_{i^\mu}$). Changes in soil and solution concentrations can be attributed to equilibrium sorption and reversible (kinetic) or irreversible sorption or transformation. Various forms of the advection/dispersion equation have been tailored to specific assumptions regarding these processes, different methods of parameter estimation, and different experimental conditions.

The multireaction and transport model (MRTM) is a form of the advection/dispersion equation containing expressions for equilibrium and kinetic sorption, and irreversible sorption and transformation processes (Selim, Xue, and Iskandar 1995). The MRTM is given as:

The Freundlich equilibrium equation

$$S = K_f C^b \tag{2}$$

where

S = amount of solute retained by soil, μg/g

K_f = distribution coefficient, cm^3/g

b = dimensionless (typically $b < 1$)

A reversible (nonlinear) kinetic reaction equation

$$\frac{\partial S_k}{\partial t} = \frac{\theta}{\rho} k_1 C^n - k_2 S_k \tag{3}$$

where

S_k = solute fraction adsorbed and/or chemically bound to soil particle surfaces, μg/g soil

k_1 and k_2 = associated rate coefficients (hr^{-1}, for $n = 1$)

n = order of reaction (dimensionless)

and, an expression for irreversible solute removal

$$\Psi = \rho \frac{\partial S_{irr}}{\partial t} = k_{irr}\theta C \tag{4}$$

where

Ψ = retention sink term, μg/cm^3·hr

S_{irr} = solute fraction irreversibly removed by precipitation/dissolution, transformation, and immobilization (irreversible sorption), μg/g soil

k_{irr} = associated rate coefficient, hr^{-1}

The complete mix model is another modification of the advection/ dispersion equation developed for thin-disk columns, employed with highly reactive contaminants for which breakthrough curves cannot be obtained using conventional length columns (Myers et al., In Preparation; Townsend, Myers, and Adrian 1995). Hydrodynamic dispersion is assumed to be negligible, and the concentration inside the cell is assumed to be equal to the concentration exiting the cell (D and $\partial C/\partial z$ are equal to zero). The Townsend, Myers, and Adrian (1995) model assumes linear equilibrium sorption ($S = K_f C$), which gives

$$\rho \frac{\partial S}{\partial t} = \rho K_f \frac{\partial C}{\partial t}$$

and a first-order reaction expression, which for complete mix gives

$$\mu C = \sum \gamma_i$$

where

μ = TNT transformation rate coefficient, hr^{-1}

γ_i = accumulation term for breakdown product i, mg/ℓ·hr

The general form of the complete mix equation given these assumptions is (Townsend, Myers, and Adrian 1995)

$$C = \frac{C_o}{1 + \theta_H \mu n} \left[1 - e^{\left[-\frac{\left(\frac{1}{\theta_H} + \mu n \right)}{n + \rho K_d} t \right]} \right]$$

(5)

where

C = effluent solute concentration, mg/ℓ

C_o = influent solute concentration, mg/ℓ

θ_H = hydraulic residence time, hr

μ = transformation rate constant, hr^{-1}

n = porosity

ρ = bulk density, kg/ℓ

K_d = distribution coefficient, ℓ/kg

Review of several studies utilizing the above models indicates that model fit and parameter estimation is case specific and multivariate (Table 1). Previous studies suggest that a correlation exists between K values and clay content, organics content, cation exchange capacity (CEC), and soil mineralogy (Pennington and Patrick 1990; Kaplan and Kaplan 1982a,b; Hale et al 1979; Ainsworth et al. 1993). Consistent parameter ranges attributable to these factors are not readily apparent here (Tables 1, 2, and 3).

For the studies listed in Table 1, model parameters were estimated by a variety of methods, including fitting data from batch studies with an equilibrium equation, such as the Freundlich (Equation 2). In transport experiments on contaminated and uncontaminated soils (Comfort et al. 1995), distribution coefficients (K_f, sometimes referred to as nonlinear K_d) and Freundlich exponent were determined from TNT adsorption isotherms at 24 hr retention time. Other studies have indicated that this does not generally give good correspondence to data obtained from column studies (Selim, Xue, and Iskandar 1995). Parameter values given in Table 1 appear to support this, with distribution coefficients estimated from batch studies typically higher than those indicated by column studies. In miscible displacement studies, Selim, Xue, and Iskandar (1995) found that model parameters based on batch adsorption data for linear, Freundlich, Langmuir, and modified Langmuir equilibrium models provided poor fit to TNT soil column breakthrough curves, with the exception of a reference clay for which a linear model corresponded well to the data (see Table 1). Both TNT arrival times and peak concentrations were

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Table 1
Comparison of TNT Distribution and Transformation Rate Coefficients for Previous Studies

Soil	Sorption Parameters		Transf Rate Coefficient	Model/Conditions
	K, ℓ/kg	b	μ^a, hr^{-1}	
Townsend, Myers, and Adrian (1995)				
WES silt	4.5	1.0	0.025	• Thin-disk study • Complete mix model • 1st order reaction expression • Linear equilibrium sorption • C_{TNT} = 60 mg/ℓ
Yokena clay	10	1.0	0.013	
Ottowa sand	1.5	1.0	0.008	
Selim, Xue, and Iskandar (1995)				
Kolin (LAAP) • pH 4.4 • 10.6% clay • CEC 16.3 cmol$_c$/kg			0.043 (K_{irr})	• Stop flow study • 500 μM Ca(NO$_3$) background solution • Multireaction transport model (MRTM) • C_{TNT} = 0.01 mg/ℓ
Reference clay • 1:9 bentonite/sand • CEC 75 cmol$_c$/kg	0.203	1.0		• Miscible displacement study • Methanol background solution (50% in distilled water) • Linear model • Limited retardation • Near 100% TNT recovery • C_{TNT} = 0.1 mg/ℓ
Same	3.69^b	0.841^c	0.084 (k_{irr})	• Miscible displacement study • 500 μM Ca(NO$_3$) background solution • MRTM • Highly retarded • 35% TNT recovery • C_{TNT} = 0.01 mg/ℓ

[a] Decay constants reflect both degradation and irreversible sorption.
[b] Batch experiments for bentonite soil indicated a K of 6.59 ℓ/kg (Xue, Iskandar, and Selim 1995).
[c] Estimated from batch isotherm. No known method for independently estimating the empirical constant.
[d] SOM = Soil Organic Matter.

(Sheet 1 of 3)

Table 1 (Continued)

Soil	Sorption Parameters		Transf Rate Coefficient	Model/Conditions
	K, ℓ/kg	b	μ^a, hr^{-1}	
Selim, Xue, and Iskandar (1995)				
Norwood • pH 7.4 • 18% Silt • 3% Clay • SOM 0.32%[d] • CEC 4.1 cmol$_c$/kg	9.54 to 9.61	0.526	0.138 (k$_{irr}$)	• Miscible displacement study • 500 μm Ca(NO$_3$)$_2$ background solution • MRTM • C$_{TNT}$ = 0.01-0.1 mg/ℓ
Same	1.98		0.05 (k$_{irr}$)	• Stop flow study • MRTM • C$_{TNT}$ = 0.01 mg/ℓ
Xue, Iskandar, and Selim (1995)				
Norwood soil				• Batch study - 1 day retention • Modified Langmuir best fit • 500 μM Ca(NO$_3$)$_2$ background solution • C$_{TNT}$ = 1-11 mg/ℓ
Kolin	6.17	0.566		• Batch study - 1 day retention • Freundlich best fit • 500 μM Ca(NO$_3$)$_2$ background solution • C$_{TNT}$ = 1-11 mg/ℓ
Bentonite/sand	65.9	0.841		
Comfort et al. 1995				
Contaminated soil • pH 6.51 • SOM 1.5% • CEC 12.5 cmol$_c$/kg • Silt 13% • Clay 7%				• 1-D advection-dispersion equation best fit • Freundlich nonlinear transport code

Table 1 (Concluded)

Soil	Sorption Parameters		Transf Rate Coefficient	Model/Conditions
	K, ℓ/kg	b	μ^a, hr^{-1}	
Comfort et al. 1995 (Continued)				
Sharpsburg silty clay loam (uncontaminated) • pH 5.96 • SOM 3.05% • CEC 29.1 cmol$_c$/kg • Silt 57% • Clay 32%	9.5	0.64		• Batch study • 24 hr retention time • Freundlich linear and nonlinear fits • 3 mM CaCl$_2$ background solution • C$_{TNT}$ = 0-62 mg/ℓ
Same	3.3	1.0		
Same	1.67		0.0188	• Transport study • 3mM CaCl$_2$ background solution spiked with ^{3}H$_2$O • μ values generated from linear transport model • 1-D advection-dispersion equation • Freundlich linear and nonlinear transport code • C$_{TNT}$ = 70 mg/ℓ
Same	4.8		0.105	• Transport study • 3mM CaCl$_2$ background solution spiked with ^{3}H$_2$O • 1-D advection-dispersion equation • Freundlich linear and nonlinear transport code • C$_{TNT}$ = 6.3 mg/ℓ
Same			0.0025	• μ values estimated from fit to BTCs - gave better fit to nonlinear transport model • C$_{TNT}$ = 70 mg/ℓ
Same			0.00542	• μ values estimated from fit to BTCs - gave better fit to nonlinear transport model • C$_{TNT}$ = 6.3 mg/ℓ

(Sheet 3 of 3)

Table 2
Clay, Organics, CEC, and pH for Soils From Table 1 With Similar K Values

Soil	K	Clay, %	Organics, %	CEC	pH	Batch or Transport
Norwood	9.54 to 9.61	3	0.32	4.1	7.4	Transport
Sharpsburg	9.5	32	3.05	29.1	5.96	Batch

Table 3
K Values for Clay Soils From Table 1

Soil	K	Clay, %	Organics, %	CEC	pH	Batch or Transport
Bentonite/Sand	65.9	10	0	75	U/K[1]	Batch
Bentonite/Sand	0.203	10	0	75	U/K	Transport/Methanol
Bentonite/Sand	3.69	10	0	75	U/K	Transport/$CaNO_3$
Sharpsburg	9.5	32	3.05	29.1	5.96	Batch/$CaCl_2$
Kolin	6.17	10.6			U/K	

[1] Unknown or not given.

overpredicted. Retardation in column studies may also be influenced by high
flow rates resulting in nonequilibrium conditions. Under these conditions,
TNT could appear to be nonreactive (for a nonreactive solute, a C/C_o value of
0.5 is achieved at V/V_o value of approximately 1) (Selim, Xue, and Iskandar
1995).

Comfort et al. (1995) estimated the degradation constant μ by two meth-
ods: fitting the linear transport model and a first order degradation model to
the TNT breakthrough curves. The latter method gave the best fit to the data
for a nonlinear sorption model. For the assumptions of the complete mix
model, an analytical solution based on zero order production and first order
degradation also exists for estimation of μ (Chapter 3 Results and Discussion).
Comfort et al. (1995) suggest that there is a concentration dependence of TNT
degradation and irreversible sorption, and that in this case a first order decay
equation may not be an adequate descriptor.

Several studies (Comfort et al. 1995; Selim, Xue, and Iskandar 1995; Xue,
Iskandar, and Selim 1995) have shown that singularity and linearity are not
always valid assumptions in modeling TNT sorption. The hysteretic behavior
observed in some studies listed in Table 1 supports this. Xue, Iskandar, and
Selim (1995) examined the equilibrium sorption of TNT and RDX in batch
studies. All TNT isotherms were nonlinear (Table 1). Comfort et al. (1995)
suggest also that TNT mobility may be underestimated if a linear model is
defined using low concentrations since in highly contaminated soils, solute
concentrations approaching effective solubility limits may increase mobility
and violate the assumption of linearity. However, in transport studies of

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layered contaminated/uncontaminated soil, Comfort et al. (1995) also concluded that the sorptive capacity of the subsoil can reduce TNT solution concentrations to the point that linear sorption is applicable.

TNT breakdown products and mechanisms

In numerous column studies, production of TNT breakdown products have been correlated with declining TNT concentrations, evidence of TNT reduction within the column (Selim, Xue, and Iskandar 1995; Xue, Iskandar, and Selim 1995; Pennington and Patrick 1990; Townsend, Myers, and Adrian 1995). Breakdown products frequently reported are 2-amino-dinitrotoluene (2A-DNT) and 4-amino-dinitrotoluene (4A-DNT) (Figure 1). Nitrobenzene, benzene, 2,6-dinitrotoluene (2,6-DNT), and 1,3,5-trinitrobenzene (TNB) have also been reported.
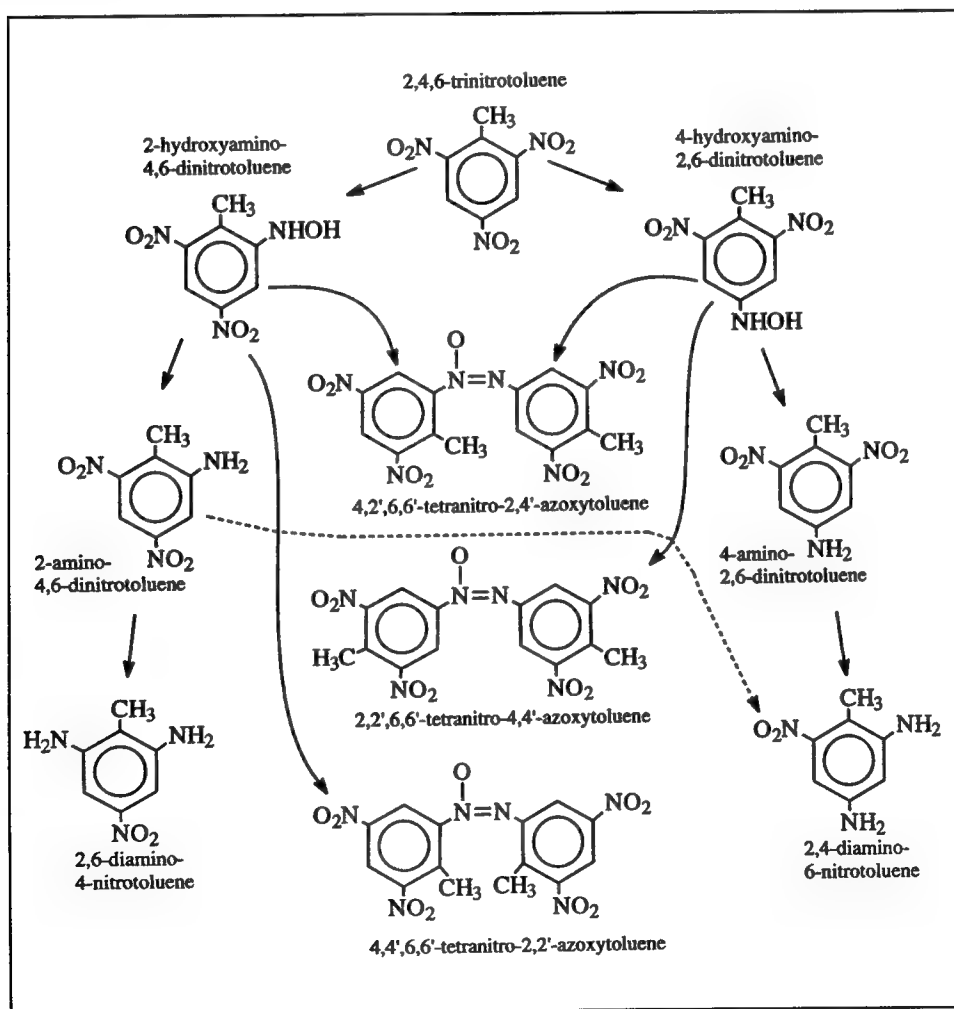
Figure 1.   In situ degradation pathways of TNT (McGrath 1995, after Kaplan and Kaplan 1982c and Kaplan and Kaplan 1983)

Amino breakdown products are formed by both biotic and abiotic processes (Comfort et al. 1995), and many soil minerals are capable of catalyzing nitro-to-amino reduction reactions. 2,6-dinitrotoluene (2,6-DNT) may be present as an impurity of TNT in the influent. TNB is a photolytic breakdown product and is not thought to be produced in the columns.

Higher production of 4A-DNT than 2A-DNT has been reported in several studies (Comfort et al. 1995; Pennington and Patrick 1990; Townsend, Myers, and Adrian 1995). Biotic reduction of the nitro group in the para position may be responsible for formation of greater amounts of 4A-DNT than 2A-DNT. Comfort et al. (1995) observed greater relative production of amino-dinitrotoluenes at lower TNT concentrations, which may be a result of the toxicity of TNT to microbes at higher concentrations.

Effect of pH and redox potential (Eh)

Little has been reported regarding the influence of reduction potential on TNT transformation, perhaps because of the difficulty in making accurate determinations of Eh. Boopathy, Wilson, and Kulpa (1993) studied anaerobic removal of 100 ppm TNT under different electron-accepting conditions. Highest removal (82 percent) was seen for nitrate-reducing conditions. Sulfate-reducing conditions resulted in 35-percent removal. For H_2CO_2 methanogenic conditions, removal was approximately 35 percent. No TNT degradation was observed when there was no other electron acceptor present (acetotrophic conditions), indicating that TNT reduction was likely achieved by cometabolism (no bacterial growth was observed under these conditions) and TNT was not utilized as an electron acceptor. While anaerobic bacteria are capable of reducing TNT to amino intermediates, toxicity of these compounds may preclude or inhibit further biological breakdown. This would support the assumption of a multimechanistic breakdown process in soils.

Highly reducing conditions appear to favor TNT reduction. Price, Brannon, and Hayes (1995) studied the combined effects of pH and Eh on reduction of TNT in a spiked soil. Only two breakdown products, 2A-DNT and 4A-DNT, were observed at all Eh/pH combinations. From 0 mV to -150 mV, 2,6-diamino-4-nitrotoluene (2,6-DANT) and 2,4-diamino-6-nitrotoluene (2,4-DANT) were observed and were present at all pH at -150 mV. TNT was persistent only under oxidizing or moderately reducing (0 mV) conditions at pH 6 or below. This is consistent with the observations of Folsom et al. (1988), who correlated decreasing TNT recovery with increasing soil pH. In column studies of Norwood and Kolin soils (Xue, Iskandar, and Selim 1995), higher sorption of the Norwood soil was also attributed to higher pH.

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Study Objectives

The objective of this study was to obtain TNT and TNT transformation product breakthrough curves for Louisiana Army Ammunition Plant (LAAP) soils in thin-disk soil columns in an anaerobic environment. The results of this study will be compared with those obtained in a previous study (Townsend, Myers, and Adrian 1995), using thin-disk columns in an aerobic environment, to identify any differences in transformation products and preferred breakdown pathways.

2   Materials and Methods

Soil

Four soils from LAAP were used in this study. They were selected to give a representative cross section of physical properties. Soils A and B are predominantly sandy, with comparable hydraulic conductivity (Table 4). Soil C has approximately two times the clay/silt content of A and B, and hydraulic conductivity three orders of magnitude lower. Soil D is predominantly clay and silt, with hydraulic conductivity below measurable limits. Geotechnical analysis, including specific gravity (SG) and particle size distributions for all four soils, are given in Figures 2, 3, 4, and 5.

Table 4 Soil Properties					
Soil	SG	Depth, ft	Sand, %	Fines, %	Hydraulic Conductivity, cm/s
LAAP-A	2.66	8-11	73.3	26.7	3.17E-04
LAAP-B	2.68	12-15	74.0	26.0	2.97E-04
LAAP-C	2.70	4-7.5	59.0	41.0	7.75E-07
LAAP-D	2.74	7.5-11.5	22.1	77.9	<1E-09

Thin Disks

Experiments were conducted in stainless steel columns (Figure 6) 0.32 cm in length, with a 4.45-cm ID. Stainless steel porous plates (0.64 cm thick, 100-μm nominal pore diameter, Mott Metallurgical, Farmington, CT) were placed on the inlet and outlet sides of the soil layer. These plates were used to distribute flow across the soil surface. Rubber O-rings were used to seal the end caps. The end caps were connected to stainless steel inlet and outlet tubing, selected to eliminate sorption by the tubing and to exclude light.
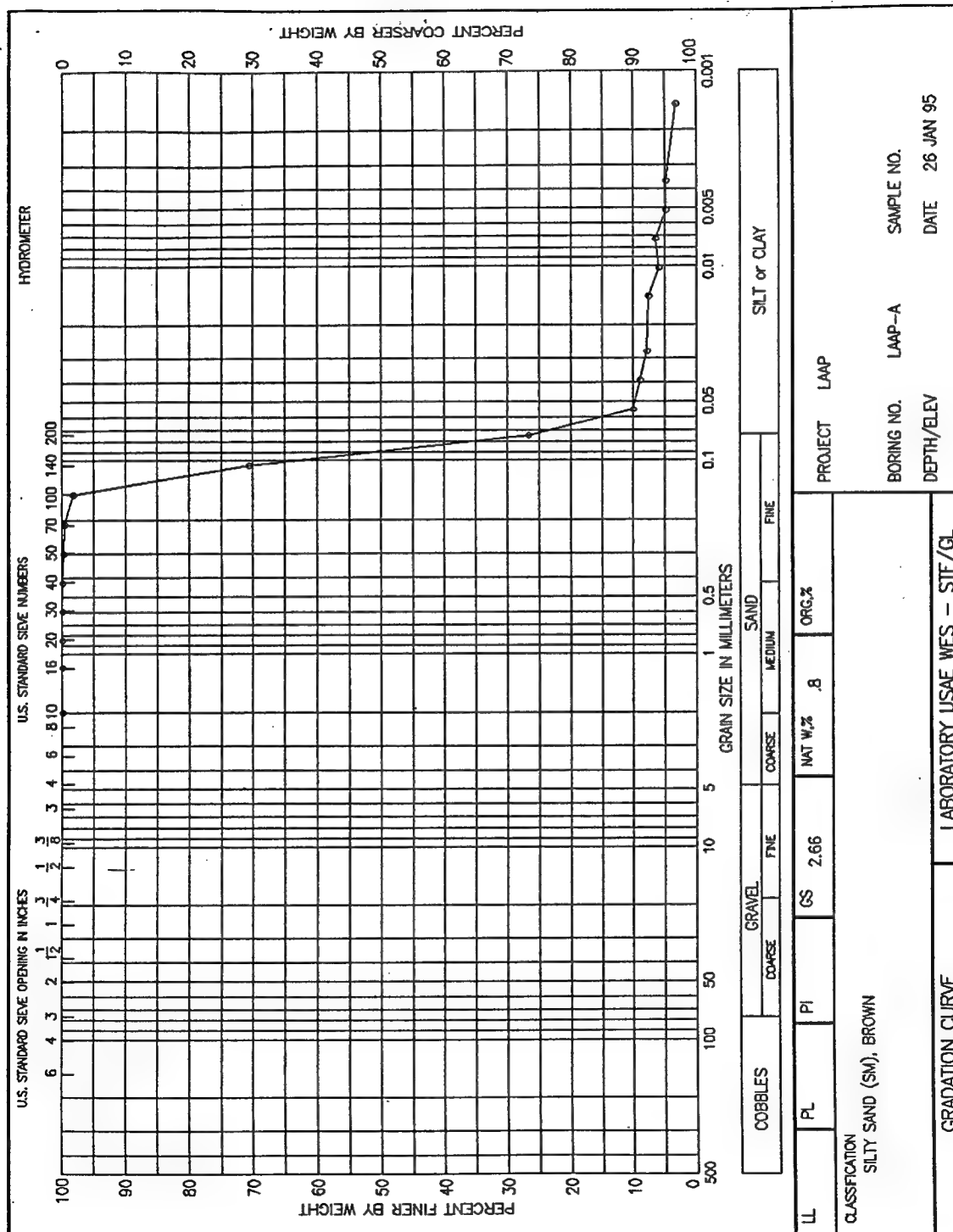
Figure 2.   Gradation curve - LAAP-A
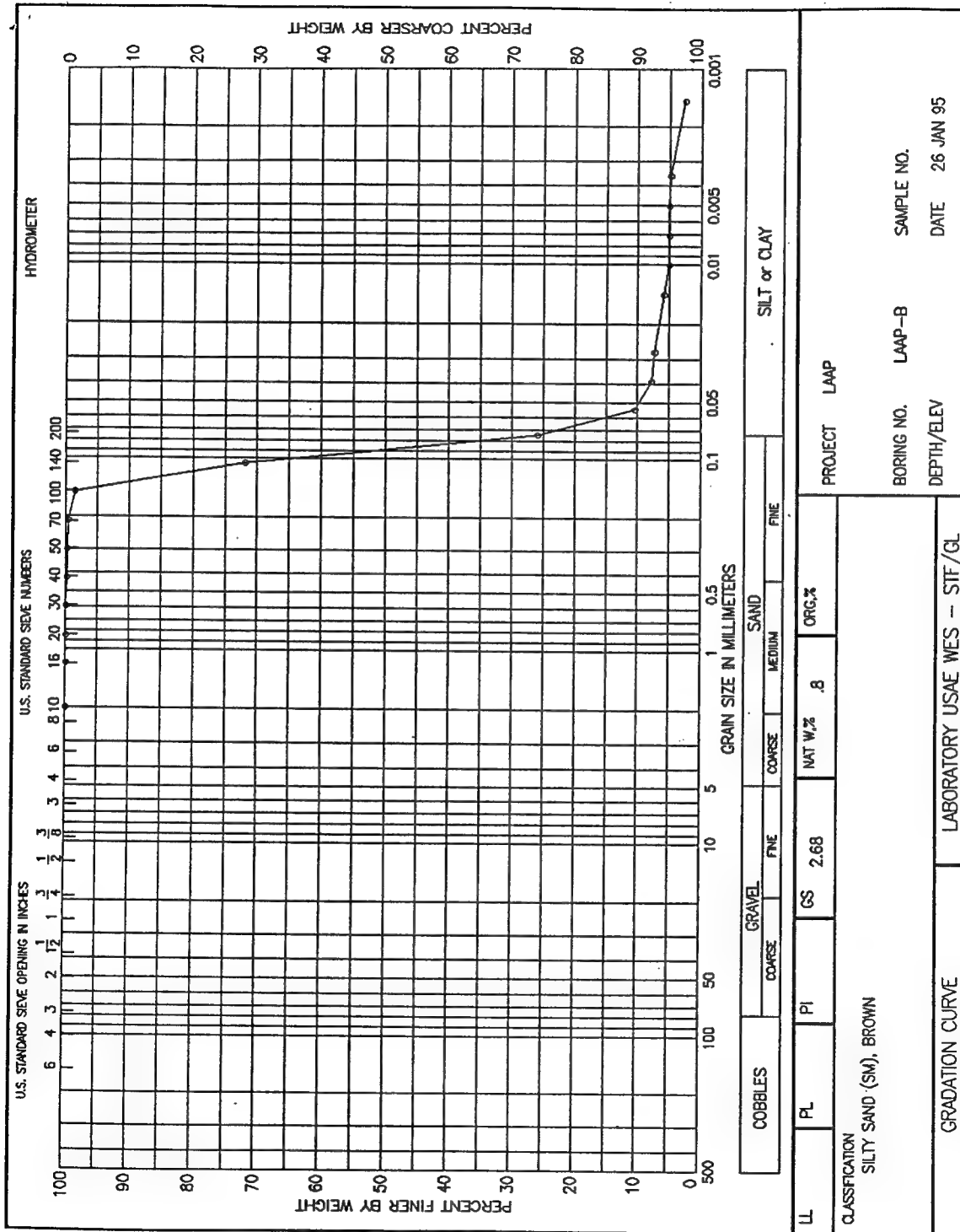
Figure 3. Gradation curve - LAAP-B
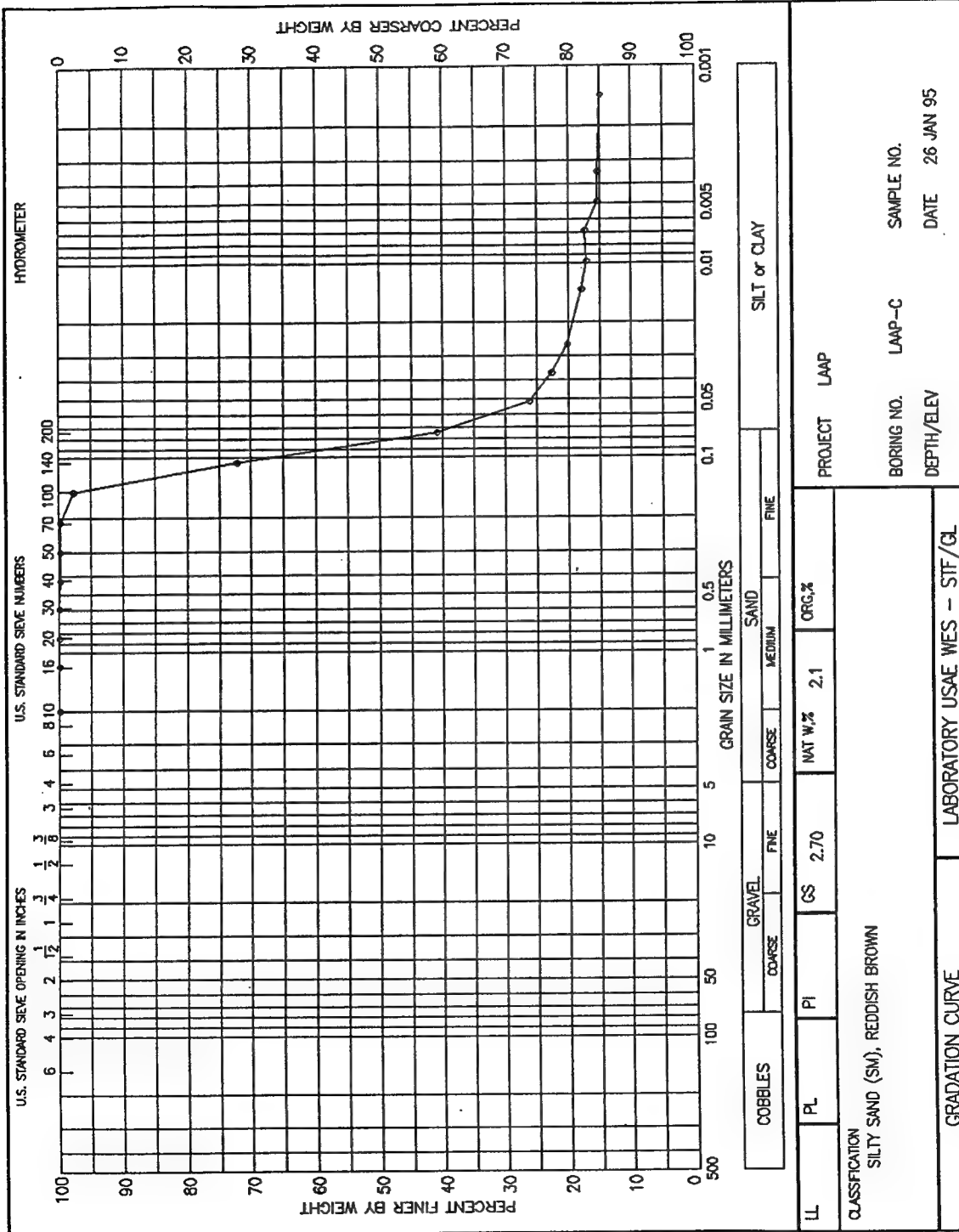
Figure 4. Gradation curve - LAAP-C
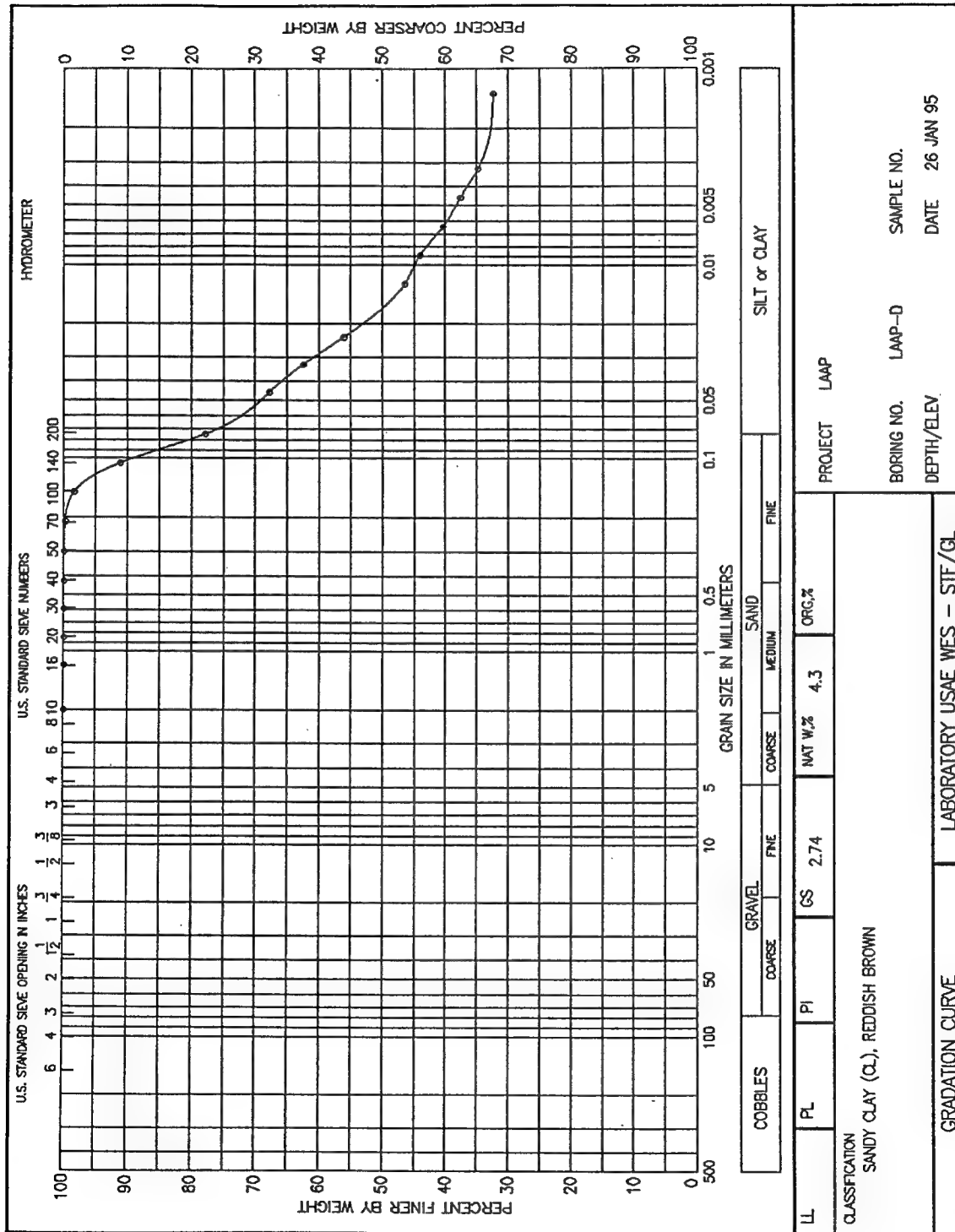
Figure 5. Gradation curve - LAAP-D
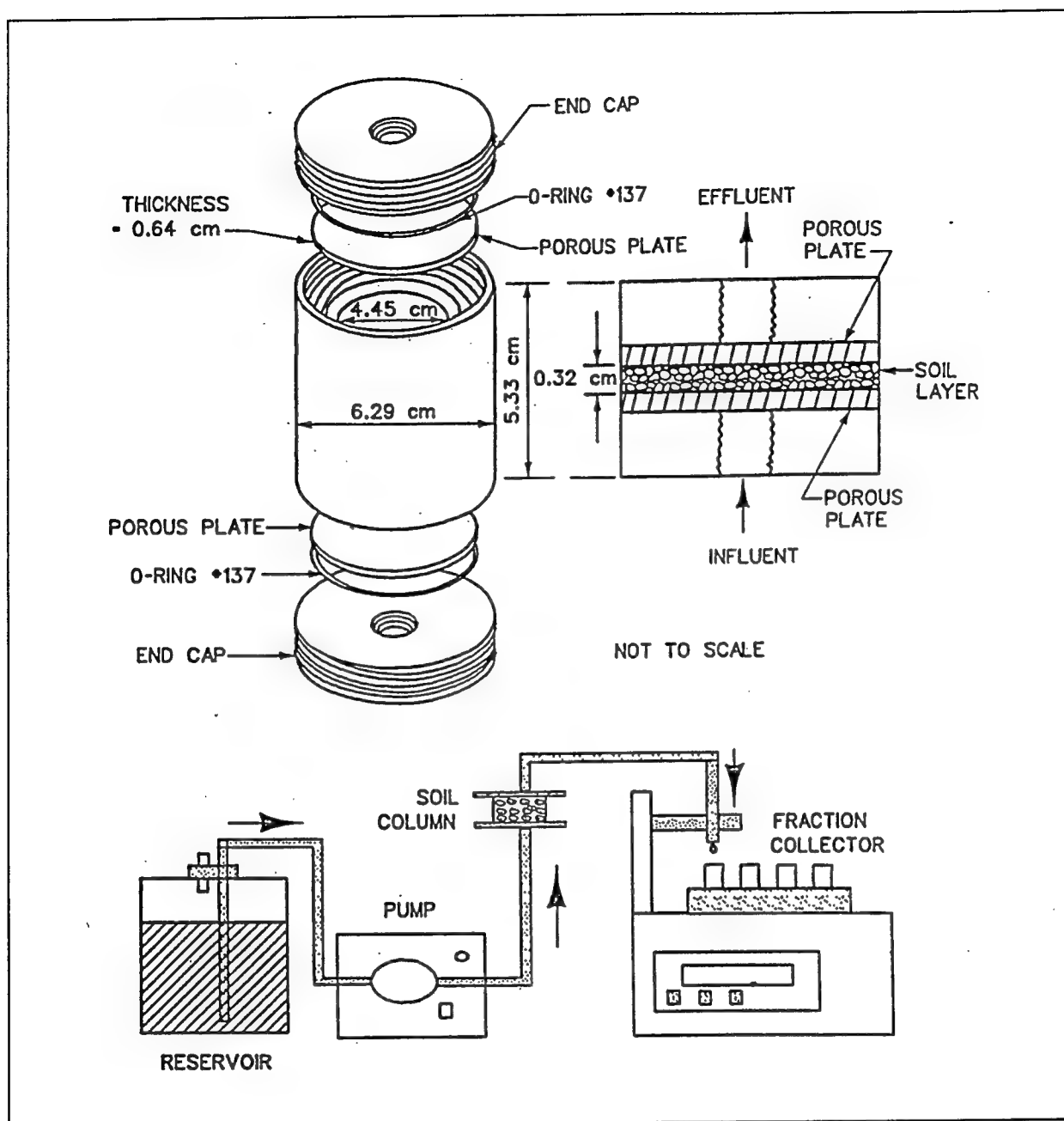
Figure 6.   Thin-disk schematic and experimental apparatus

Pumps and Flow Rates

Constant volume metering pumps (Model QG6-2-SSY, Fluid Metering, Inc., Oyster Bay, NY) were used to pump water through the columns in upflow mode. Target flow rates were initially in the range of 1/100 of the saturated hydraulic conductivity for each of the columns (10^{-4} to 10^{-9} cm/s), in order to match flow rates expected in concurrent hydraulic flume tests.

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However, flow rates this low (5.62E-07 mL/hr to 17.8E-02 mL/hr) could not be achieved with these pumps. The pumps were set to the lowest flow rate possible, yielding approximately 1 mL/hr, with variation of approximately ± 0.2 mL/hr.

Glove Box

A plexiglass glove box was constructed to accommodate a nitrogen distribution system, four columns and fraction collectors, and supplies necessary to collect and preserve samples within the glove box (Figures 7 and 8).
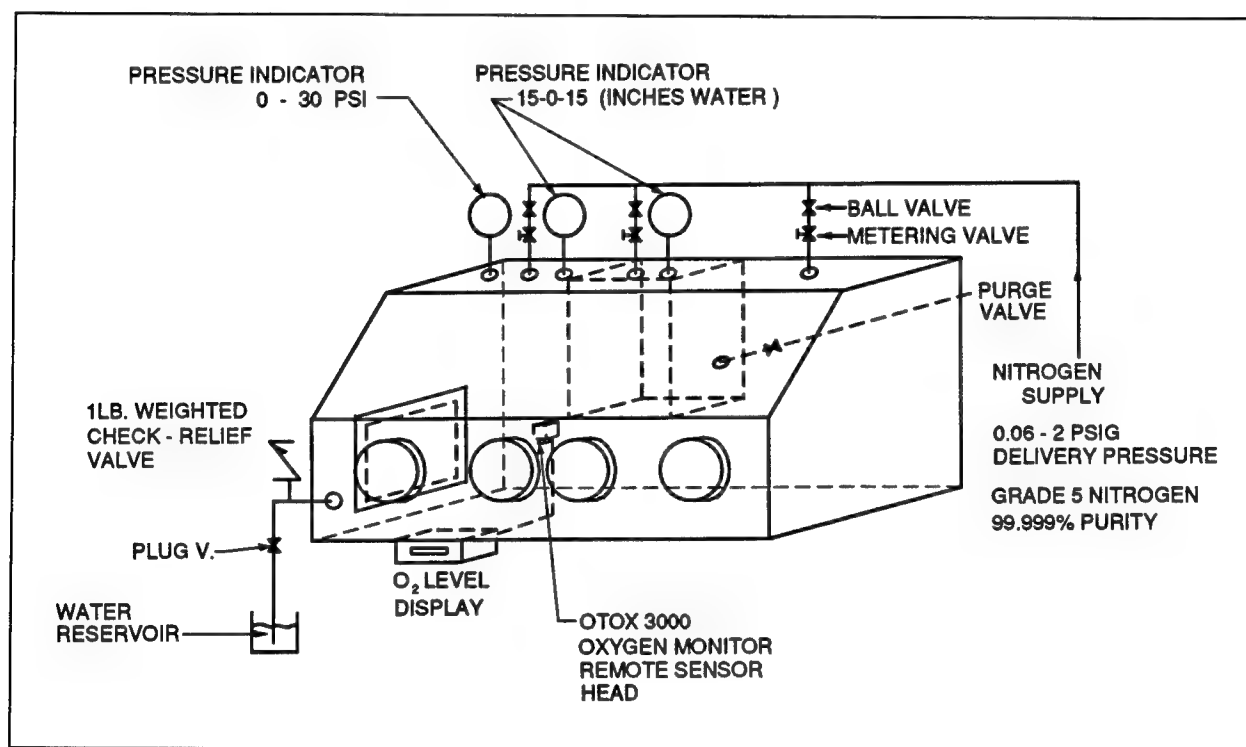
Figure 7.   Positive pressure glove box

Column Loading

Columns were loaded outside of the glove box by one of two methods, the "sand method" or the "slurry method." In the sand method, the column is filled three-fourths full with de-aired distilled deionized (DDDI) water. Soil at the in situ water content is weighed into a beaker, then sprinkled into the column and allowed to settle as the column is drained. After draining, the column is tapped lightly on a flat surface so the consolidated soil completely fills the cell between the porous plates, giving a soil layer approximately
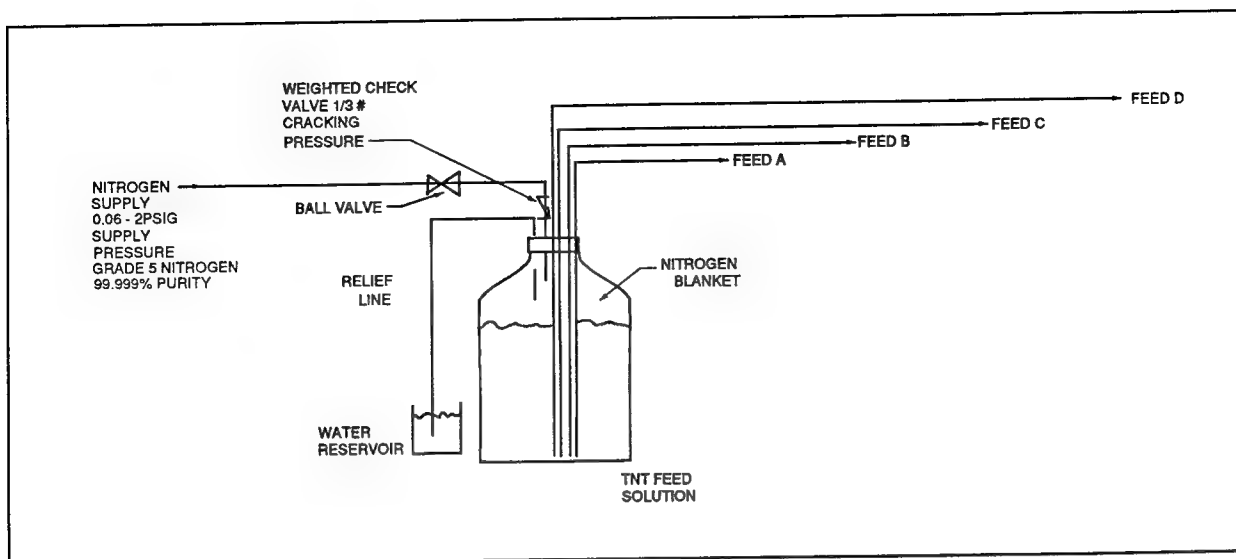
Figure 8. Glove box nitrogen distribution system

0.32 cm in depth (Figure 6). The mass of soil in the column is calculated by weight difference of the beaker. In the slurry method, the column and insert are filled approximately one-third to one-half full with DDDI water. A slurry of DDDI water and soil is then added and the column drained. The column is tapped to consolidate the soil layer, as for the sand method. Soil mass is estimated as for the sand loading method. Soil and column parameters are given in Table 5.

Table 5
Soil and Column Parameters

Soil	Wt, g	V_t, cm^3	w	Solids SG g/cm^3	n	ρ_b g/cm^3
LAAP-A	7.5064	4.93	0.008	2.66	0.43	1.511
LAAP-B	7.5105	4.93	0.008	2.68	0.44	1.511
LAAP-C	6.4889	4.93	0.021	2.70	0.52	1.289
LAAP-D	4.9810	4.93	0.043	2.74	0.65	0.969

Note: W_t = weight of soil in column, measured at natural moisture content, i.e., "wet" weight; V_t = volume of column; w = natural water content, dimensionless, given by: $w = W_{water}/W_{soil}$; SG = specific gravity; n = porosity, dimensionless, given by: $n = 1 - (W_t/(V_t \cdot (w+1) \cdot SG))$; ρ_b = bulk density, given by: $\rho_b = W_t/(V_t \cdot (w+1))$.

- LAAP-A - "Column A" was loaded with 7.5064 g (at in situ water content - wet weight) LAAP-A soil by the sand method.

- LAAP-B - "Column B" was loaded with 7.5105 g wet weight LAAP-B soil using the sand method.

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- LAAP-C - "Column C" was loaded with 6.4889 g wet weight LAAP-C soil using the slurry method at approximately 10:1 water-to-solids ratio.

- LAAP-D - "Column D" was loaded with 4.9810 g wet weight LAAP-D soil using the slurry method at approximately 10:1 water-to-solids ratio. This soil has the highest fines content and could not be significantly consolidated by tapping the column.

Feed Solution Preparation

TNT feed solution was prepared in an amber glass jar by combining 4 ℓ of MilliQ water with 0.50 g of 2,4,6-trinitrotoluene (10 percent water added) (Eastman Kodak Company, Rochester, NY). The solution was stirred for 5 days, filtered and analyzed by HPLC SW-846 Method 8330. A vacuum was applied, and the solution was de-aired for approximately 30 hr and then refrigerated. The following day, it was de-aired again for 1 hr. It was then mixed with LAAP groundwater in an approximate ratio of two parts TNT solution to one part groundwater. After mixing, 5 mL was pipetted out, placed in an amber 20-mL vial, and preserved with 5 mL of acetonitrile. This was the first measured feed sample. The headspace of the jar was then purged with nitrogen before connection to the pumps.

Thin-Disk Column Tests

Pumps and tubing were purged with DDDI water prior to connection with the columns. Soil columns were loaded, then placed in the glove box and connected to the pumps and fraction collectors. The glove box was purged of air prior to commencing flow of DDDI water through the columns. After a steady-state flow rate was established, the pumps and tubing from feed to pump and pump to column were drained and primed with TNT feed solution. Flow was resumed through the columns with TNT feed solution.

Positive pressure was maintained within the glove box at 2 to 5 in.[1] of water by continuous flow of Grade 5 nitrogen into the box and maintenance of static head on the relief line. During sample handling, when technicians were working in the glove box, the nitrogen supply was shut off and pressure dropped to a comfortable working level, just above ambient. When daily sampling operations were completed, continuous nitrogen flow was resumed. Oxygen levels were monitored continuously within the glove box using factory-calibrated Neotronics Otox 3000 oxygen monitors. Oxygen levels were maintained between 0.0 and 0.1 percent throughout the experiment. Column tests were performed at room temperature (18-24 °C).

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[1] To convert inches to centimeters, multiply by 2.54.

TNT feed solution was pumped through the four columns for 504 hr, at ±0.2 mL/hr for the equivalent of the following step inputs:

Column A - 277.45 pore volumes

Column B - 357.28 pore volumes

Column C - 219.10 pore volumes

Column D - 211.09 pore volumes

At the end of the step inputs, the TNT feed solution was replaced with DDDI water. Flow was resumed with DDDI for another 330 hr or a total of the following pore volumes:

Column A - 246.32 pore volumes

Column B - 179.82 pore volumes

Column C - 219.73 pore volumes

Column D - 139.03 pore volumes

At the end of this time, the pumps were stopped. A chloride tracer study was conducted on the loaded columns, and a chloride breakthrough curve developed. The soils were then removed from the columns for analysis.

Sampling/Sample Handling

Effluent samples were collected continuously during the TNT step input and subsequent column flushing. Fraction collectors (Model UFC, Eldex Laboratories, Inc., Napa, CA) were used to collect samples continuously for 2-hr intervals. Sample volumes ranged from 1.6 to 6 mL, with 2 to 3 mL typical. The larger volumes reflect temporary aberrations in flow rate or occasional failure of the collector to advance, resulting in a longer collection interval.

Samples were preserved daily and placed in storage in an environmental chamber at 4 °C prior to analysis. Working inside the glove box, 1.5 mL eluate was pipetted from each sample bottle and preserved with an equal volume of acetonitrile. Sample bottles were capped prior to removal from the glove box to prevent intrusion of air into the headspace of the sample bottles. PTFE septas were used in sample bottle caps to prevent adsorption of contaminants by the septa. The unpreserved remainder of the samples were also removed and weighed. Total sample weight was calculated by adding 1.5 g to the measured weight to account for the 1.5 mL removed for preservation and analysis, assuming a density of 1 g/cm^3 for the eluate.

At the completion of the column study, soil was removed from the columns and stored in the dark at 4 °C until analyzed. No preservatives were added.

Chemical Analysis

Feed and eluate samples were analyzed for 2,4,6-trinitrotoluene (TNT), 1,3-dinitrobenzene (DNB), methyl-2,4,6-trinitrophenylnitramine (TETRYL), 1,3,5-trinitrobenzene (TNB), 4-amino-2, 6-dinitrotoluene (4A-DNT), 2-amino-4,6-dinitrotoluene (2A-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitro-toluene (2,4-DNT), 3,5-dinitroaniline (3,5-DNA), 2,6-diamino-4-nitrotoluene (2,6-DANT), and 2,4-diamino-6-nitrotoluene (2,4-DANT) on two independent HPLC systems using the dual column confirmation method developed by Jenkins et al. (1988), now SW-846 Method 8330. The first system consisted of a 600E system controller, a 712 Wisp Auto Injector, and a 486 Tunable Absorbance Detector (Millipore/Waters Chromatography Division, Milford, MA). The column was an HPLC-18 (Supelco 25 cm by 4.6 mm) column eluted with 1:1 methanol/water at 1.2 mL/min. The second HPLC system consisted of an HPLC Module I (Millipore/Waters Chromatography Division, Milford, MA). The column was an HPLC-CN (Supelco 25 cm by 4.6 mm) column eluted with 1:1 methanol/water at 1.2 mL/min.

Samples were analyzed for a composite of 4,2',6,6'-tetranitro-2,4'-azoxy-toluene, 2,2',6,6'-tetranitro-4,4'-azoxytoluene, and 4,4',6,6'-tetranitro-2,2'-azoxytoluene using the above method, except that the columns were eluted with 5.4:4.6 acetonitrile/water at 1.5 mL/min instead of 1:1 methanol/water at 1.2 mL/min.

Soil removed from the columns following the study was analyzed for TNB, DNB, Tetryl, TNT, 4ADNT, 2ADNT, 26DNT, 24DNT, 44'Azoxy, 26DANT, 24DANT, and 35DNA. Soil was extracted with acetonitrile using SW-846 Method 8330.

Chloride Tracer Studies

Chloride tracer studies were conducted to estimate the average hydraulic residence time of the apparatus. The point at which the measured electrical conductivity equals 50 percent of maximum is taken as the average hydraulic residence time (Freize and Cherry 1979). This factor can be used to estimate t_o, the average inlet and outlet residence time.

3 Results and Discussion

TNT Breakthrough Curves

Figure 9 illustrates hypothetical normalized breakthrough curves for a complete mix model (Townsend, Myers, and Adrian 1995). Unchanging effluent concentrations at steady state implies that the rate of adsorption equals the rate of desorption. Steady-state effluent concentrations (of TNT or breakdown products) below influent concentrations indicate a transformation
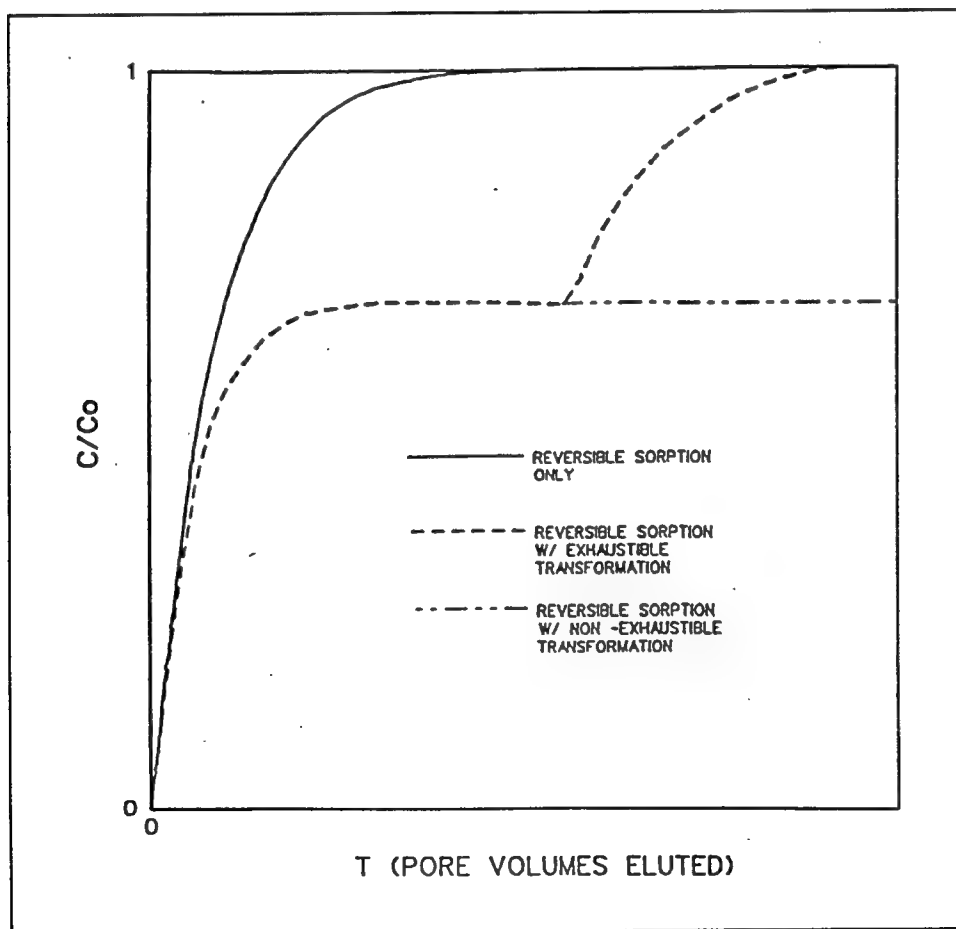
Figure 9. Normalized hypothetical breakthrough curves for complete mix

process within the soil. If the soil component responsible for this transformation is exhaustible, a delayed return to the influent concentrations should be seen.

Normalized TNT breakthrough curves generated in this study exhibit some anomalies (Figure 10). C/C_o values greater than one (1) occurred in all four columns near the end of the step input. This may be due to analytical error
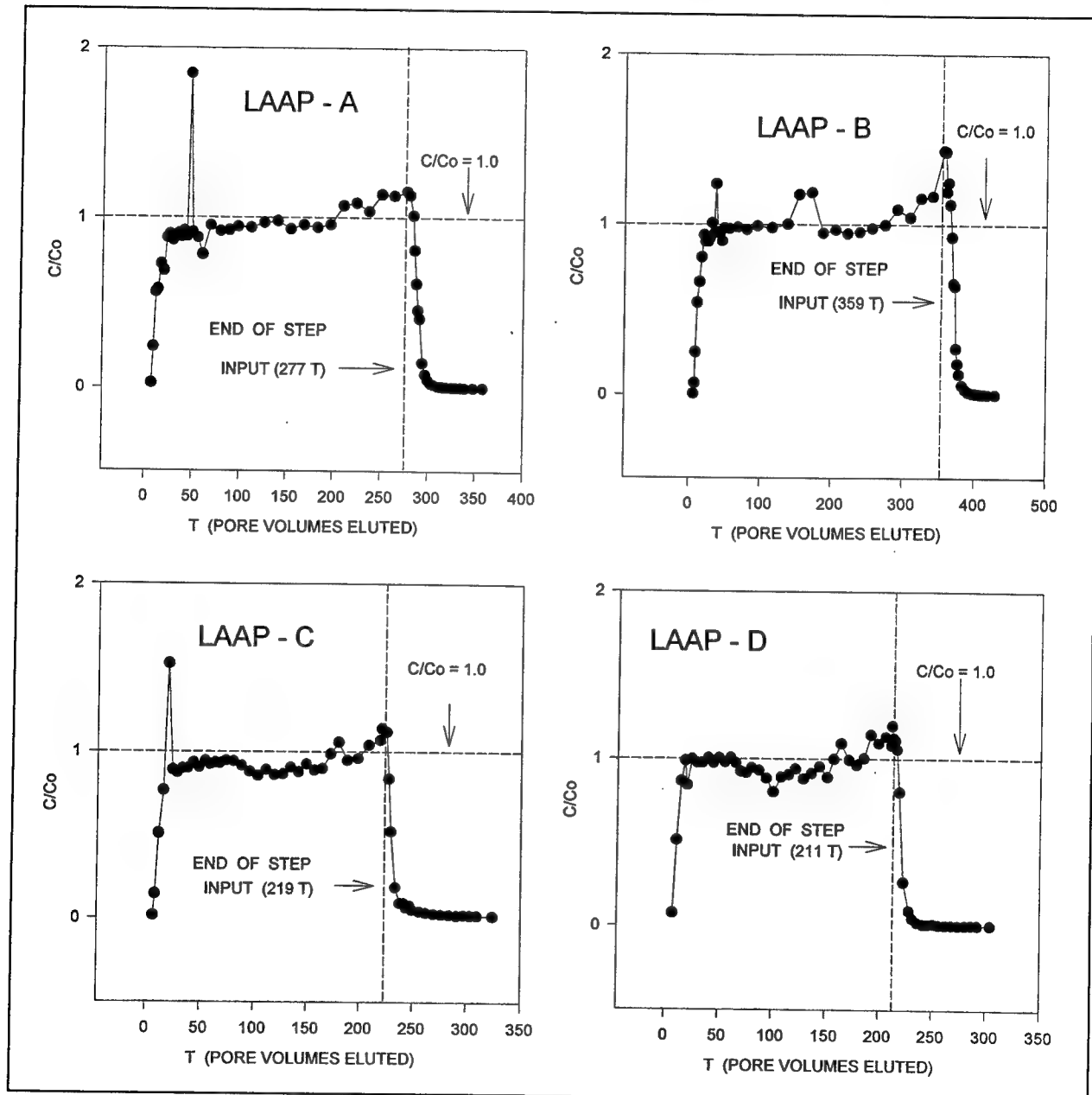
Figure 10. TNT breakthrough curves

resulting from slight inaccuracies in the dilution achieved when preserving the samples with acetonitrile. Also, the feed solution was sampled 11 times over the duration of the experiment (Appendix A Table 1A). This revealed that C_o values were not constant, declining gradually from 48.8 to 43.4 mg/ℓ over the course of the experiment. These data were fitted with a curve to extrapolate C_o values for intermediate eluate sample points. Uncertainty associated with the curve fit may also have influenced C/C_o values.

Although apparent outliers existed in the data for all four columns, the curves were essentially symmetrical in shape, indicating reversible sorption. The slope of the front and tail portions of the curves is very steep, however, indicating that the amount of sorption that occurred was very small. Steady-state concentrations near, but below, initial concentrations indicate the presence of a TNT transformation process, but the transformation rate is apparently small in these soils.

Column A (Figure 10a) reached steady state at approximately $T = 70$ pore volumes. Steady-state concentrations were approximately 95 percent of the initial TNT concentration until about $T = 210$, when eluate concentrations exceeded influent concentrations. A single outlier ($C/C_o > 1$) also occurred at $T = 47$.

Column B (Figure 10b) reached steady state at approximately $T = 50$. Steady-state concentrations were approximately 97 percent of initial concentrations. Outliers occurred at 32, 37, 138, 154, and 172 pore volumes and from 292 pore volumes to the end of the step input.

Column C (Figure 10c) reached steady state at approximately $T = 40$. Steady-state concentrations fluctuated between approximately 87 and 95 percent of initial concentrations. Eluate concentrations exceeded influent concentrations at 20 pore volumes and from 180 pore volumes to the end of the step input.

Column D (Figure 10d) reached steady state at approximately $T = 24$. Steady-state concentrations fluctuated between approximately 88 and 98 percent of initial concentrations. Eluate concentrations exceeded influent concentrations from approximately 163 pore volumes to the end of the step input.

Transformation Product Breakthrough Curves

Figure 1 illustrates one model for TNT reduction and conjugation reactions. TNB is not shown, because it is a photolysis product. Figures 11, 12, 13, and 14 are the normalized transformation product breakthrough curves for columns A,B,C, and D, respectively. Influent concentrations were below detection for all but TNT and 2,4-DNT. Influent concentrations for all other analytes were assumed to be one-half the detection limit. The transformation behavior in all four soils was similar, with the same products forming at roughly the same magnitude. The only significant products to be produced

Figure 11. Normalized transformation product breakthrough curves LAAP-A

Figure 12. Normalized transformation product breakthrough curves LAAP-B

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Figure 13. Normalized transformation product breakthrough curves LAAP-C

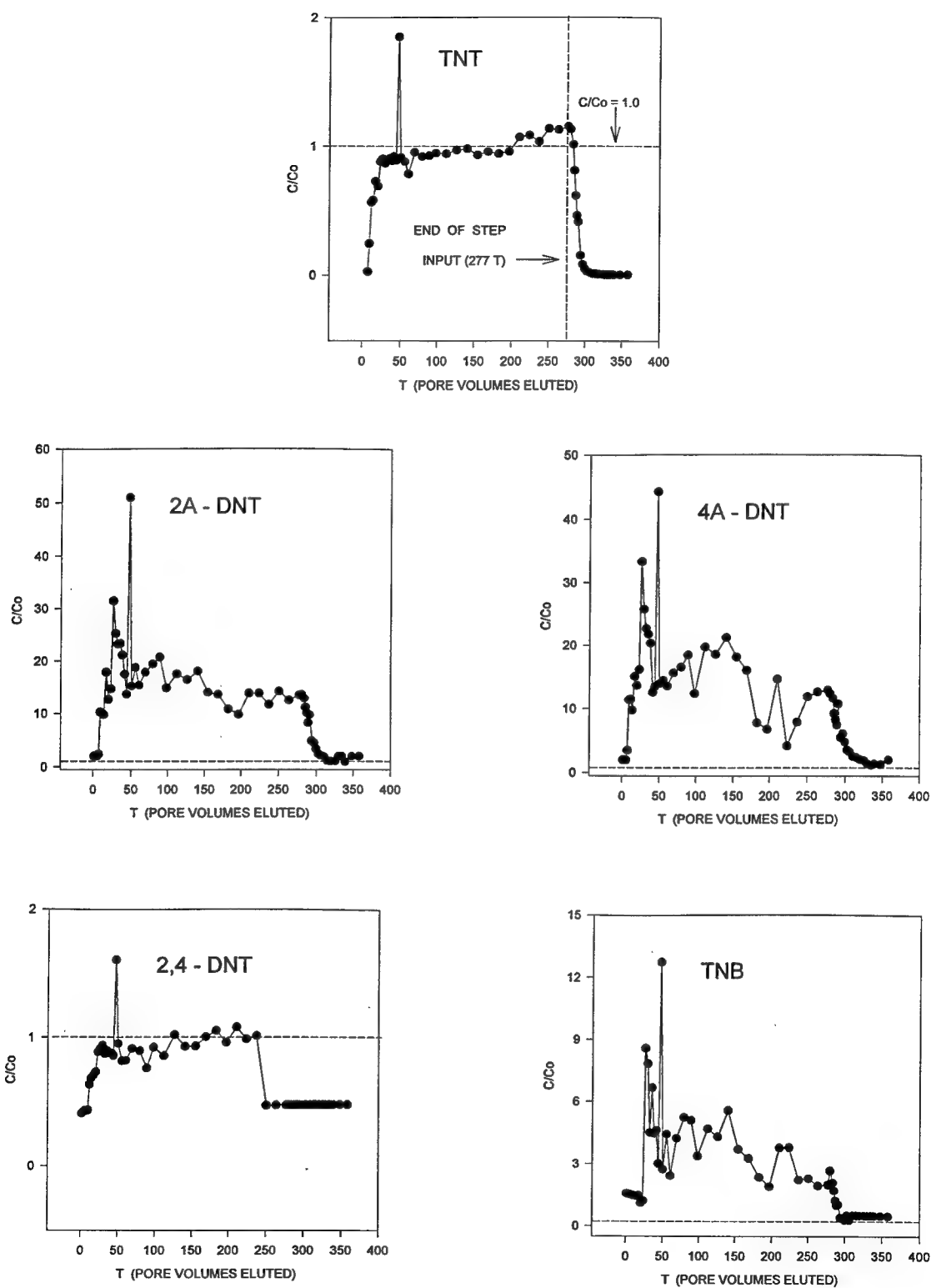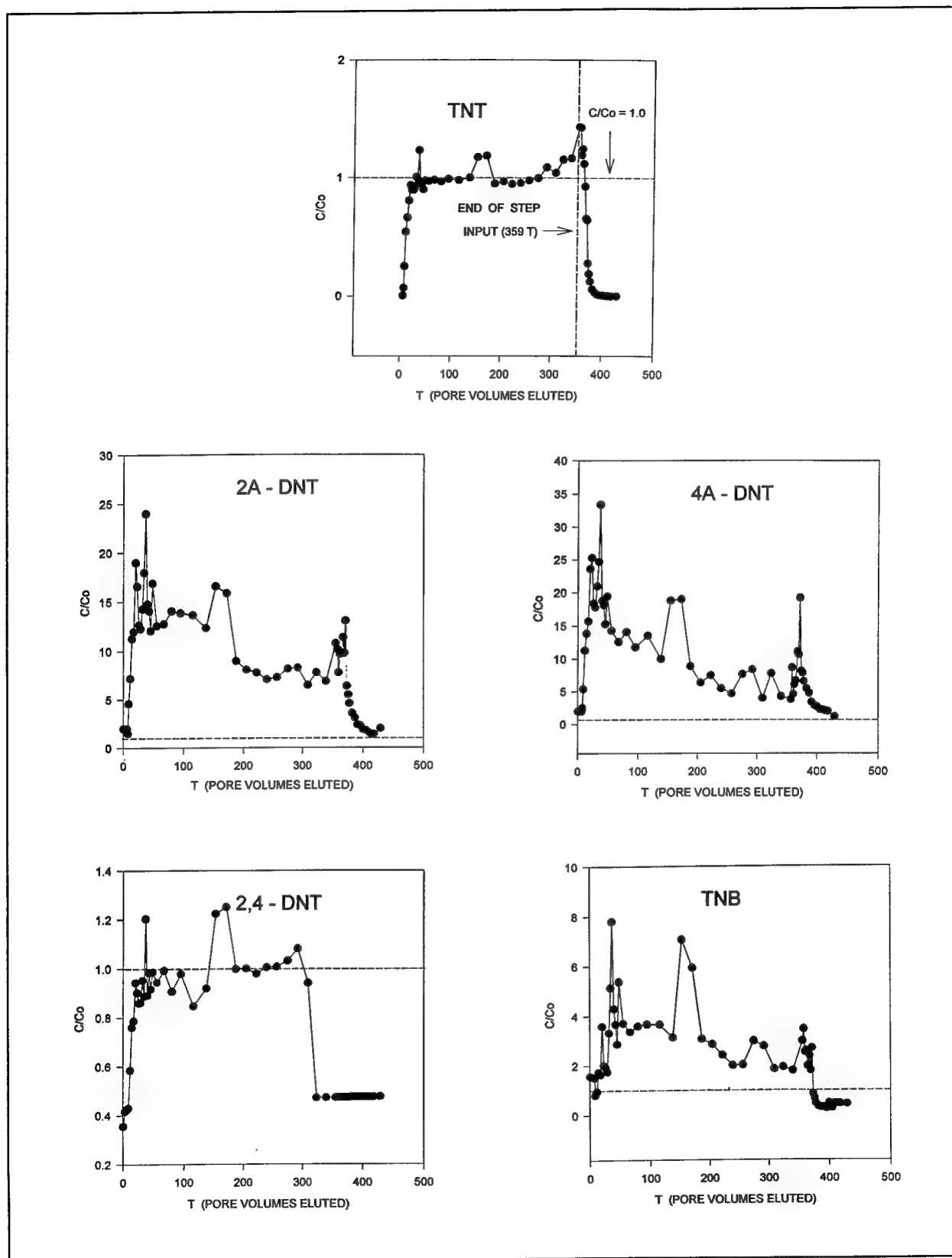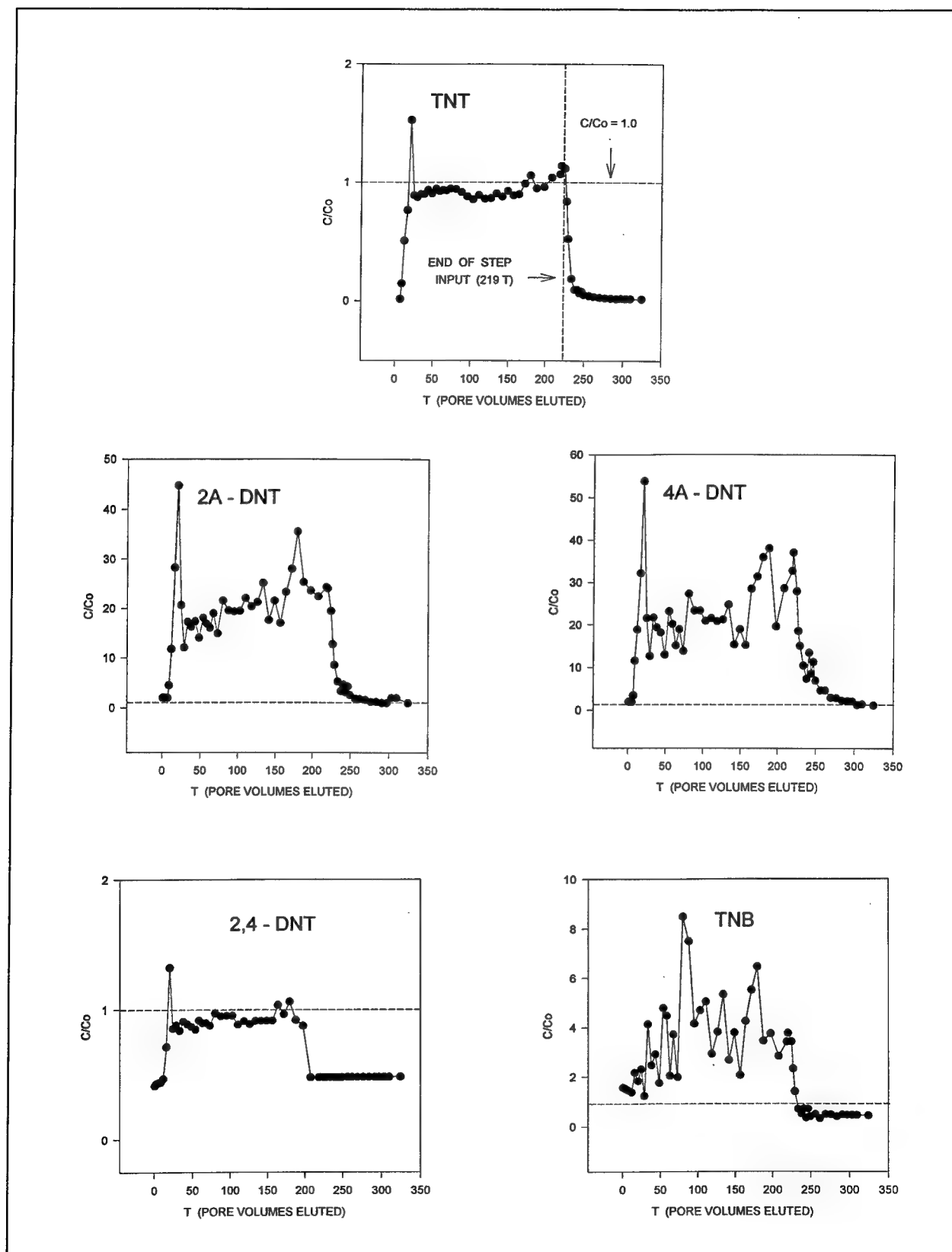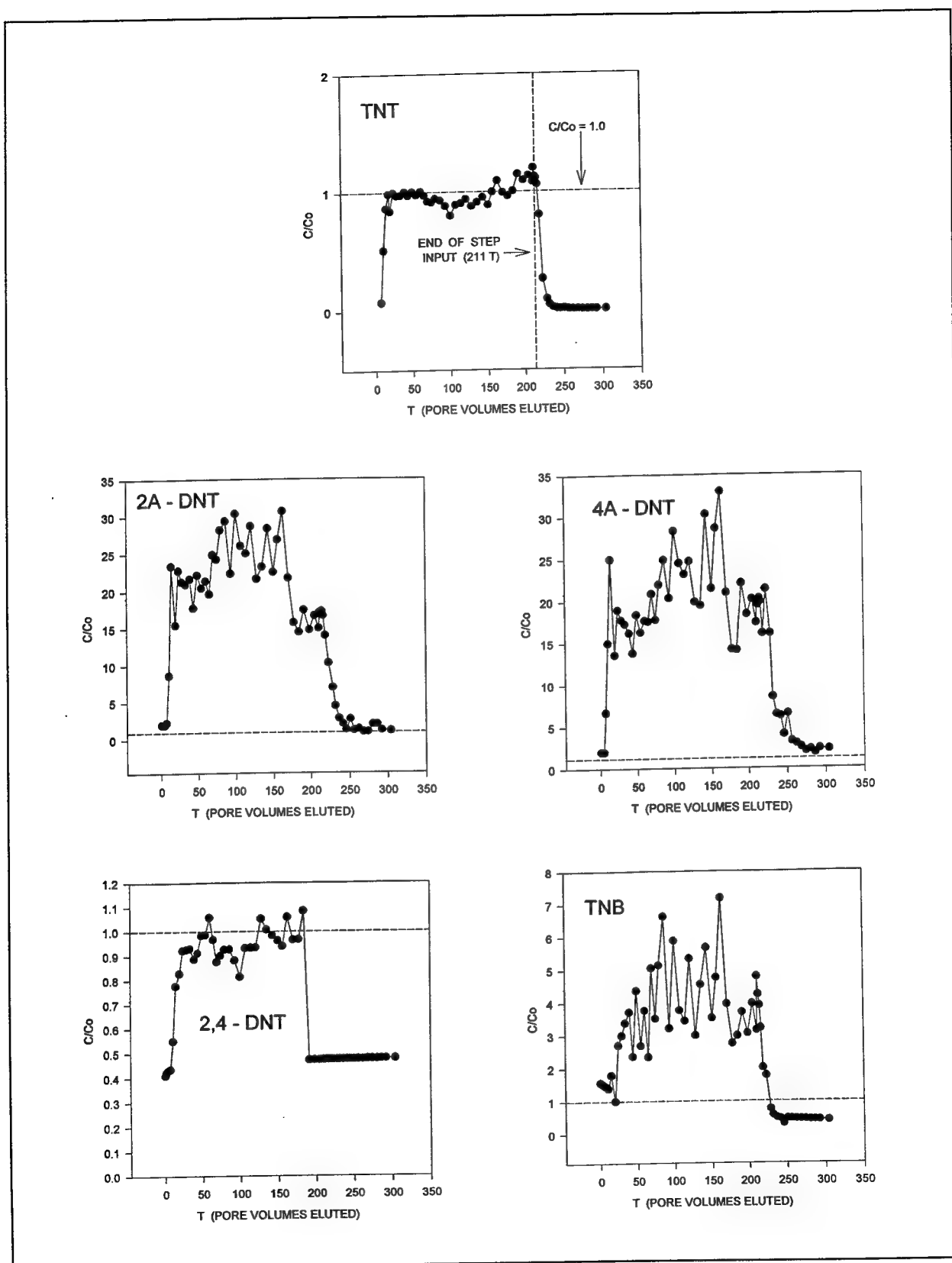Figure 14. Normalized transformation product breakthrough curves LAAP-D

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within the soil columns were 2A-DNT and 4A-DNT. TNB was also detected in the eluate but is believed to have been formed during the sample collection interval after the eluate left the columns. 2,4-DNT appeared in measurable quantities in all eluates, but the breakthrough curve did not reflect production within the column ($C/C_o < 1$). The other analytes (2,6-DANT, 2,4-DANT, 2,6-DNT, 3,4-DNA, 4,4-Azoxy, and 2,2-Azoxy) were below detection limits in the eluate. (Chemical abbreviations are identified in Appendix B.) A summary of the effluent data for the four columns is given in Table 6.

The principal breakdown products present in Column A (Figure 11) eluate were 2A-DNT and 4A-DNT. The 2A-DNT and 4A-DNT peaks at approximately $T = 47$ correlate to the TNT breakthrough curve for Column A, which also shows a concentration spike at approximately $T = 47$. Coincident peaks at $T = 47$ support the explanation for apparent outliers at this point as analytical error. The rise and fall of 2A-DNT and 4A-DNT concentrations was relatively synchronous, with 2A-DNT concentrations slightly higher than 4A-DNT. Concentrations of both breakdown products were variable throughout the study. Steady-state C/C_o concentrations for 2A-DNT were achieved at about $T = 60$ and ranged from approximately 10 to 20. C/C_o for the 4A-DNT was more variable, ranging from 3 to 21 from $T = 60$ to the end of the step input. Measurable amounts of 2,4-DNT were detected in the eluate, but C/C_o concentrations were below or just slightly above 1, with the exception of an outlier at approximately $T = 60$, as for the other analytes. This suggests that the 2,4-DNT that entered the column passed through the column without significantly breaking down further. TNB was also measurable in the eluate, with C/C_o ranging from approximately 2.5 to 6 from $T = 60$ to the end of the step input. As previously indicated, because TNB is a photolysis product, formation of TNB is believed to have occurred during the sample collection interval, after the eluate left the column, and is not reflective of a breakdown process within the soil.

C/C_o concentrations for 2A-DNT and 4A-DNT were again reasonably coincident (Column B - Figure 12). In contrast to Column A, 4A-DNT concentrations were more nearly equal to the 2A-DNT concentrations and exceeded them at some data points. C/C_o concentrations for 2A-DNT ranged from approximately 6 to 17, and for 4A-DNT ranged from approximately 3 to 19. Apparent outliers for 2A-DNT and 4A-DNT were again coincident to apparent outliers for the TNT breakthrough curve. 2,4-DNT was also detected in the eluate but again in insufficient concentrations to suggest significant formation within the column. C/C_o concentrations reached approximately 1.2 for three data points, but these corresponded to apparent outliers for the other analytes, which suggests that these concentrations were the result of analytical error rather than production of 2,4-DNT within the column. C/C_o for TNB ranged from approximately 2 to 4, excluding apparent outliers, for the steady-state interval of the step input.

2A-DNT and 4A-DNT formation in Column C (Figure 13) followed the general trends of Columns A and B. C/C_o values are slightly higher, ranging from approximately 12 to 28 for 2A-DNT, and 12 to 35 for the 4A-DNT

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Table 6
Effluent Concentrations for TNT and TNT Transformation Products (mg/ℓ)

Analyte	Column A			Column B			Column C			Column D		
	Min[1]	Max[2]	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
TNT	<MDL	45.9	23.5	<MDL	47.6	26.4	<MDL	45.1	24.5	<MDL	48.5	26.0
2A-DNT	<MDL	0.315	0.010	<MDL	0.190	0.080	<MDL	0.283	0.120	<MDL	0.304	0.140
4A-DNT	<MDL	0.334	0.010	<MDL	0.253	0.100	<MDL	0.381	0.140	<MDL	0.303	0.140
2,4-DNT	<MDL	0.045	0.020	<MDL	0.044	0.030	<MDL	0.044	0.030	<MDL	0.046	0.030
TNB	<MDL	0.130	0.040	<MDL	0.106	0.040	<MDL	0.195	0.060	<MDL	0.175	0.060

[1] MDL - Minimum Detection Limit: 0.02 mg/ℓ - TNT, 2A-DNT, 4A-DNT, 2,4-DNT, TNB.
[2] Excluding apparent outliers.

(excluding apparent outliers) during the steady-state interval of the step input. Significant 2,4-DNT formation was again not demonstrated. C/C_o ranged from approximately 2 to 9 for TNB during the steady-state interval of the step input.

Column D (Figure 14) exhibited fewer apparent outliers than the other three columns, all occurring in the last quarter of the step input. 2A-DNT and 4A-DNT trends are again coincident, with C/C_o concentrations ranging from approximately 18 to 30 for 2A-DNT, and from 13 to 30 for 4A-DNT during the steady-state interval of the step input. No significant formation of 2,4-DNT was demonstrated. C/C_o concentrations for TNB ranged from approximately 2 to 7 for the steady-state interval, excluding apparent outliers.

Soil Concentrations

Soils used in the column study were clean soils for which site monitoring indicated a negligible risk of contamination. Analysis of the soil from each column after the transport experiments were conducted resulted in nondetect values for all analytes except for 44' Azoxy in LAAP Column D. A value of 1.24 mg/kg was found for this analyte. Since 44' Azoxy did not appear in the eluate, this breakdown product may have been strongly sorbed.

Transformation Product Distribution

Analysis of the transformation product distribution is usually taken from the mole balance. Because few transformation products were formed, a mole balance was not calculated. Since this was not done, a quantitative comparison cannot be made. However, there were only three transformation products produced in measurable concentrations. The third, TNB, is not considered to have been a product of processes within the column and is therefore not of interest in the transformation product distribution. 4A-DNT and 2A-DNT are the remaining two transformation products. The concentrations and trends of these two analytes were relatively synchronous for all four columns. Qualitatively, they appear to have been produced in amounts of approximately equal magnitude.

Complete-Mix Analytical Model

In the Townsend, Myers, and Adrian (1995) study, a complete-mix model was developed for the thin-disk breakthrough curves in order to elucidate the TNT transport process. The complete mix model and similar assumptions developed in the Townsend, Myers, and Adrian (1995) study were used in this study. The model used is similar to one derived by Skopp and McCallister (1986). In a complete-mix model, hydrodynamic dispersion is neglected. The

concentration inside the cell is assumed to be equal to the concentration exiting the cell.

The Townsend, Myers, and Adrian (1995) model includes linear equilibrium sorption and a first-order reaction expression. From conservation of mass (Equation 6) and a linear sorption isotherm (Equation 7), Equation 8 is derived for the initial condition where $C(0) = 0$ (Townsend, Myers, and Adrian 1995).

$$QC_o - QC - \mu nVC = nV\frac{dC}{dt} + \rho V\frac{dS}{dt} \tag{6}$$

$$S = K_d C \tag{7}$$

$$C = \frac{C_o}{1 + \theta_H \mu n}\left[1 - \exp\left[-\frac{\theta_H^{-1} + \mu n}{n + \rho K_d} \, t\right]\right] \tag{8}$$

where

C = effluent solute concentration, mg/ℓ

C_o = influent solute concentration, mg/ℓ

θ_H = hydraulic residence time, hr

μ = transformation rate constant, hr^{-1}

n = porosity

ρ = bulk density, kg/ℓ

K_d = distribution coefficient, ℓ/kg

t = time, hr

Equation 8 is the basic equation describing reactive, sorptive contaminant transport through a complete-mix soil system. This equation has several practical limitations. For instance, difficulties arise in taking measurements directly at the soil layer boundary. In general, columns have an inlet and an outlet associated with them, which are usually not part of the main model. Therefore, the solute must first travel through the inlet portion of the column before coming into contact with the soil layer and, upon leaving the soil layer, must travel through an outlet before being collected for analysis. In traditional columns, the inlet and outlet travel time is usually much smaller than the residence time in the soil, and is often neglected. With thin-disk columns,

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the inlet and outlet residence times are significant and therefore must be considered.

$$C = \frac{C_o}{1 + \theta_H \mu n} \left[1 - e^{\left[- \left[\frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} \right] (t - t_o) \right]} \right] \qquad (9)$$

where t_o is the inlet-outlet residence time (hours).

Equation 9 describes solute travel through the complete thin-disk apparatus during the step input of the feed solution.

After the end of the feed solution step input, DDDI water was pumped through to wash out the disk. Changing the conditions at the inlet to $C = 0$ for $t > t_1$ yields:

$$C = C_{t_1} e^{\left(- \left[\frac{\frac{1}{\theta_H} + \mu n}{n + \rho K_d} \right] (t - t_1) \right)} \qquad (10)$$

where

C_{t1} = effluent concentration at time t_1

t_1 = time at end of step input plus t_o

It is sometimes useful to represent contaminant transport through porous media as a function of the number of pore volumes eluted instead of a function of time. In order to do this, the following relationship is used:

$$T = \frac{ut}{L} \qquad (11)$$

where

T = pore volumes eluted

L = column length, cm

u = average pore water velocity, cm/s

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Parameter Estimation

Inlet and outlet residence time (t_o)

The model must be modified to account for inlet and outlet residence time in order to obtain good correspondence with the breakthrough curves. There are several possible approaches to estimating t_o. One method of determining t_o is to conduct a chloride tracer study. The time at which the measured electrical conductivity reaches 50 percent of maximum is taken to be the average hydraulic residence time of the apparatus ($\theta_{\text{H-apparatus}}$) (Freize and Cherry 1979). An estimate for t_o can also be obtained by fitting a curve (no t_o adjustment) to the experimental data (C/C_o versus T) with estimated values for μ, and K_d. t_o (or T_o) can then be estimated from the graph as the offset of the curve from the data on the T axis. A third method of estimating t_o is by dividing the measured inlet and outlet volume of each apparatus by the average flow rate for the column. This method gave the best correspondence to the data.

Transformation rate coefficient μ

Transformation rate coefficient μ (hour^{-1}) can be estimated by fitting a curve to the data, adjusting values for K_d and μ to obtain the best fit. Variations in μ will influence the approach of the curve to C_o ($C/C_o = 1$). Because transformation of TNT was limited, μ is too small to significantly affect C/C_o for TNT. Since some transformation products were formed, however, another approach to estimating μ was employed, based on the theoretical relationship:

$$D\frac{d^2C}{dX^2} - V\frac{dC}{dX} - \mu C + \gamma = 0 \tag{12}$$

For the complete mix model, the first two terms are equal to zero. For $\gamma = \text{AVG}(\Sigma\gamma_i)$ this gives:

$$\mu C = AVG[\sum \gamma_i] \tag{13}$$

where

μ = TNT transformation rate coefficient, hr^{-1}

$C = C_o$ = influent TNT concentration, mg/ℓ (which may be constant, or may vary over the time of the study)

γ_i = accumulation term for breakdown product i, mg/ℓ/hr = sample concentration/collection interval

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For this study, only three breakdown products were seen: 2A-DNT, 4A-DNT, and TNB. Because TNB is a photolysis product not produced in the soil, the average μ was estimated based only on 2A-DNT and 4A-DNT concentrations for each column, as follows:

$$\mu = AVG \left(\frac{\sum \dfrac{C_{2A-DNT}}{C_{O-TNT}} + \sum \dfrac{C_{4A-DNT}}{C_{O-TNT}}}{2} \right) \tag{14}$$

where C/C_o values are paired. Values obtained by this method were small (0.0131-0.0081 hr^{-1}), indicating little transformation of TNT. This gave good correspondence to the data.

Distribution coefficient K_d

Distribution coefficient K_d was estimated by fitting a curve to the TNT breakthrough data after a value for μ was calculated. Values obtained for K_d were small (ranging from 1.0 to 2.0 ℓ/kg), indicating little retardation or retention. Correspondence to the data is reasonably good.

Limitations of the Data

The decline of TNT concentration in the feed solution was unexpected and is not attributed to chemical or biological breakdown since the appearance of breakdown products in the feed solution was insufficient to account for the TNT loss. Although the solution was below saturation values for TNT, the use of groundwater to make up the solution may have diminished the solubility and resulted in precipitation losses. Analytical error for both feed solution and eluates could also have been responsible for varying C/C_o values.

Because TNT is not produced in the column, eluate TNT concentrations should never exceed influent concentrations. Yet, the normalized data resulted in C/C_o values > 1. Analytical error due to incorrect dilution during sample preservation is one possible cause of this disparity, as described previously. The predicted C_o values could be another source of error because the feed solution was not sampled continuously as was the eluate. The C/C_o factor is therefore heavily dependent upon the accuracy of the TNT curve fit from which predicted C_o values were obtained.

The presence of TNB in the eluate is indicative of photolytic reactions that would not have occurred within the soil. TNB is formed by the loss of the methyl group from TNT, without transition through any of the breakdown products illustrated in the transformation pathway diagram (Figure 10). Since TNB is formed after the eluate leaves the column, and forms directly from

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TNT rather than from another breakdown product, the only eluate concentration potentially affected is the TNT concentration. Thus, the formation of TNB may have resulted in depressed C/C_o values, which were nevertheless greater than 1 for portions of the study.

Discussion of Results

Production of breakdown products and retardation of TNT was small for all soils in this study, indicating minimal biological activity and limited reactivity under the anaerobic conditions studied. For Columns A and B, a clear lag in return to influent concentrations was not demonstrated, but the production of 2A-DNT and 4A-DNT appeared to decline somewhat over the duration of the step input. This would suggest that a transformation process occurred initially, but diminished during the period of the study, possibly due to exhaustion of an abiotic soil component. Columns C and D demonstrated steady to increasing transformation product production. This could suggest a stronger biotic component, possibly with associated biological population and product increases. Because measured concentrations of all analytes increased in the last quarter of the step input, the possible influence of analytical error cannot be discounted in evaluating the trend of increasing transformation product concentrations.

TNT breakdown products were distributed principally between 2A-DNT and 4A-DNT. These were produced in amounts of approximately equal magnitude. Previous studies (Kaplan and Kaplan 1982a) indicated that the preferred breakdown pathway appears to be 4A-DNT. That does not appear to be supported for these soils under these conditions. The 4A-DNT pathway has been associated with biotic transformation. The presence of equal amounts of 2A-DNT may suggest the presence of both biotic and abiotic transformation mechanisms in these soils if abiotic transformation favors 2A-DNT formation. A limited biotic transformation component is consistent with the effect of high TNT concentrations on biological activity and growth observed by Comfort et al. (1995).

Sorption appears to have been minimal and reversible for all analytes except 4,4' azoxytoluene, which was detected as a soil residual (Column D) but which did not appear in measurable concentrations in the eluate.

Distribution coefficients (1-2 ℓ/kg) were consistent with values estimated using the complete mix model by Townsend, Myers, and Adrian (1995) for sand (1.5 ℓ/kg), but were smaller than the values for silt (4.5 ℓ/kg) and clay (10 ℓ/kg), even though four different soil types were represented in this study. Distribution coefficients estimated by Selim, Xue, and Iskandar (1995) using the MRTM model were comparable (1.98 ℓ/kg) in stop flow studies on the Norwood soil (3 percent clay, 0.32 percent organics), but were higher in continuous flow studies using the MRTM model for the Norwood soil (9.6 ℓ/kg) and clay (3.69 ℓ/kg). A comparable distribution coefficient (1.6 ℓ/kg) was observed by Comfort et al. (1995) using the Freundlich model

for a silty clay loam. Soils having the closest distribution and transformation coefficients to the four LAAP soils studied are described in Table 7. One interesting result is the low K_d value for the LAAP-D soil, which had the highest proportion of fine material (77.9-percent silt and clay). Batch studies with a 1:9 bentonite/sand soil mixture (Xue, Iskandar, and Selim 1995) yielded a K_d of 65.9, and the thin-disk study conducted on Yokena clay (34-percent clay, 64-percent silt) yielded a K_d value of 10 (Townsend, Myers, and Adrian 1995). However, K_d values for the Sharpsburg soil (32-percent clay, 57-percent silt) ranged from 1.67 to 9.5 for transport and batch studies, respectively (Comfort et al. 1995). This is illustrative of the difficulty in identifying trends in TNT transport for differing soils.

Under reducing conditions, 2,6-DANT and 2,4-DANT could be expected at all pH values (Price, Brannon, and Hayes 1995). Although the present study was conducted in an anaerobic environment, only 2A-DNT and 4A-DNT were detected in the eluate. All soil residual concentrations were below detection, with the exception of a very low concentration of 44' azoxy in the soil in Column D. Since pH and Eh data were not available, the reason for persistence of TNT in these soils is not clear.

Table 7
Soils With Comparable Distribution and Transformation Coefficients to the LAAP Soils of the Current Study

Soil	pH	TOC, %	CEC	Sand, %	Silt, %	Clay, %	K_d	μ	Model/Conditions
Norwood[1]	7.4	0.32	4.1	79	18	3	1.98	0.05	MRTM Stop flow study 500 μM CaNO3 background solution C_{TNT} = 0.01 mg/ℓ
Ottowa Sand[2]				92.5	7.5	0	1.5	0.008	Complete mix Thin-disk study C_{TNT} = 60 mg/ℓ
Sharpsburg[3]	5.96	3.05	29.1	11	57	32	1.67	0.0188	1-D advection/dispersion equation with Freundlich linear and nonlinear transport code Transport study 3mM CaCL$_2$ background solution spiked with ^{3}H$_2$O μ estimated from linear transport model C_{TNT} = 70 mg/ℓ
Sharpsburg[3]	5.96	3.05	29.1	11	57	32		0.0025	1-D advection/dispersion Transport study μ estimated from breakthrough curves C_{TNT} = 70 mg/ℓ
LAAP-A[4]				73.3	26.7		1.0	0.00927	Complete mix Thin-disk study Anaerobic environment C_{TNT} ≈ 50 mg/ℓ
LAAP-B[4]				74.0	26.0		2.0	0.00807	
LAAP-C[4]				59.0	41.0		2.0	0.0131	
LAAP-D[4]				22.1	77.9		1.0	0.0131	

1 Selim, Xue, and Iskandar (1995).
2 Townsend, Myers, and Adrian (1995).
3 Comfort et al. (1995).
4 Current study.

4 Conclusions and Recommendations

The reactivity of TNT in these soil columns appears to be small. Comparisons of this study to previous studies are difficult to make because these were conducted with different soils, under different conditions, and fitted with different models. However, the data from this and previous studies can be examined for general trends in distribution and rate coefficients as a function of soil type, TNT concentration, model parameters, and type of study (batch versus transport). No consistent trends were noted for any of these parameters.

The complete-mix model provided a good fit to the thin-disk elution data in the four LAAP soils studied. TNT, under anaerobic conditions, can be expected to be persistent and mobile, as evidenced by the limited transformation of TNT and sorption demonstrated (small μ and K_d). In future studies, closer estimation of parameters may be possible with more frequent sampling of the feed solution and protection of samples from light during the sample collection interval, to prevent TNB formation.

Because little transformation or sorption occurred, conventional columns could potentially be used in transport studies with these soils. This should result in a greater difference between C and C_o at steady state, facilitating estimation of the parameter μ. In future studies, more accurate model parameters could be obtained with more frequent feed solution sampling, giving more consistent estimates for C_o between data points and possibly eliminating instances where $C/C_o > 1$. Also, protection of samples from light during collection should prevent TNB formation outside the cell. Although it is thought that TNB derives directly from TNT, rather than from an intermediate breakdown product, this would help to clarify the relative distribution of TNT and transformation products in the eluate.

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References

Ainsworth, C. C., Harvey, S. D., Szecsody, J. E., Simmons, M. A., Cullinan, V. I., Resch, C. T., and Mong, G. H. (1993). "Relationship between the leachability characteristics of unique energetic compounds and soil properties," Final Report, Project Order No. 91PP1800, U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, Frederick, MD.

Boopathy, R., Wilson, M., and Kulpa, C. F. (1993). "Anaerobic removal of 2,4,6-trinitrotoluene (TNT) under different electron accepting conditions: Laboratory study," Water Environment Research, May/June 1993, 65(3), 271-275.

Comfort, S. D., Shea, P. J., Hundal, L. S., Li, Z., Woodbury, B. L., Martin, J. L., and Powers, W. L. (1995). "TNT transport and fate in contaminated soil," *Journal of Environmental Quality* 24, 1174-1182.

Folsom, B. L, Pennington, J. C., Teeter, C. L., Barton, M. R., and Bright, J. A. (1988). "Effects of soil pH and treatment level on persistence and plant uptake of 2,4,6-trinitrotoluene," Technical Report EL-88-22, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Freize, R. A., and Cherry, J. A. (1979). *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, NJ.

Jenkins, T. F., Miyares, P. H., and Walsh, M. E. (1988). "An improved RP-HPLC method for determining nitroaromatics and nitramines in water," CRREL Report 88-23, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Kaplan, D. L., and Kaplan, A. M. (1982a). "Thermophilic biotransformations of 2,4,6-trinitrotoluene under simulated composting conditions," *Applied and Environmental Microbiology* 44(3), 757-760.

_____. (1982b). "2,4,6-trinitrotoluene-surfactant complexes: Decomposition, mutagenicity, and soil leaching studies," *Environmental Science and Technology* 16(9), 566-571.

Kaplan, D. L., and Kaplan, A. M. (1982c). "2,4,6-trinitrotoluene-surfactant complexes, biodegradability, mutagenicity, and soil leaching studies," Technical Report NATICK/TR-82/006.

_____. (1983). "Reactivity of TNT and TNT-microbial reduction products with soil components," Technical Report NATICK/TR-83/041.

McGrath, C. J. (1995). "Review of formulations for processes affecting the subsurface transport of explosives," Technical Report IRRP-95-2, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Myers, T. E., Brannon, J. M., Pennington, J. C., Townsend, D. M., Davis, W. M., Ochman, M. K., Hayes, C. A., and Myers, K. F. "Laboratory studies of soil sorption/transformation kinetics for explosives," Technical report in preparation, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Pennington, J. C., and Patrick, W. H., Jr. (1990). "Adsorption and desorption of 2,4,6-trinitrotoluene by soils," *Journal of Environmental Quality* 19, 559-567.

Price, C. B., Brannon, J. M., and Hayes, C. A. (1995). "Transformation of 2,4,6-trinitrotoluene under controlled Eh/pH conditions," TR-IRRP-95-5, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Selim, H. M. (1992). "Modeling the transport and retention of inorganics in Soils," *Adv. Agron.*, Academic Press, 47, 331-384.

Selim, H. M., Xue, S. K., and Iskandar, I. K. (1995). "Transport of 2,4,6-trinitrotoluene and hexahydro-1,3,5-trinitro-1,3,5-triazine in soils," *Soil Science*, November, 160(5), 328-339.

Skopp, J., and McCallister, D. (1986). "Chemical kinetics from a thin disc flow system: Theory," *Soil Science Society of America Journal* 50(3), 617-623.

Townsend, D. M., Myers, T. E., and Adrian, D. D. (1995). "2,4,6-trinitrotoluene (TNT) transformation/sorption in thin-disk soil columns," Technical Report IRRP-95-4, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Xue, S. K., Iskandar, I. K., and Selim, H. M. (1995). "Adsorption-desorption of 2,4,6-trinitrotoluene and hexahydro-1,3,5-triazine in soil," *Soil Science* 160, 317-327.

Bibliography

Hinz, C. (1992). "Sorption, kinetics, and transport of selected heavy metals in soil: A laboratory study and modelling approaches," Ph.D. diss., Louisiana State University, Baton Rouge.

Leggett, D. C. (1985). "Sorption of military explosive contaminants on bentonite drilling muds," CRREL Report 85-18, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

McCormick, N. G., Feeherry, F. E., and Levinson, H. S. (1976). "Microbial transformation of 2,4,6-trinitrotoluene and other nitroaromatic compounds," *Applied and Environmental Microbiology* 31(6), 949-958.

Selim, H. M., Amacher, M. C., and Iskandar, I. K. (1990). "Modeling the transport of heavy metals in soils," CRREL Monograph 2, U.S. Government Printing Office.

Selim, H. M., and Iskandar, I. K. (1994). "Sorption-desorption and transport of TNT and RDX in soils," CRREL Report 94-7, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Tchobanoglous, G., and Schroeder, E. D. (1985). *Water quality.* Addison-Wesley Publishing Company, Reading, MA.

Tucker, W. A., Dose, E. V., Gensheimer, G. J., Hall, R. E., Pollman, C. D., and Powell, D. H. (1985). "Evaluation of critical parameters affecting contaminant migration through soils," Final Report for the U.S. Army Toxic and Hazardous Materials Agency, ESE, Gainesville, FL.

Appendix A
Feed Solution Concentrations

Table A1
Measured Feed Solution Concentrations (mg/ℓ)

Day	TNB	TNT	4A-DNT	2A-DNT	2,6-DNT	2,4-DNT	2,6-DANT	2,4-DANT	DNA	4,4'-AZOX	2,2'-AZOX
1	<0.020	47.5	<0.020	<0.020	<0.020	0.059	<0.100	<0.200	<0.020	<0.500	<0.500
3	<0.020	48.8	<0.020	<0.020	<0.020	0.045	<0.100	<0.200	<0.020	<0.500	<0.500
5	<0.020	48.0	<0.020	<0.020	<0.020	0.044	<0.100	<0.200	<0.020	<0.500	<0.500
7	0.022	48.6	<0.020	<0.020	<0.020	0.041	<0.100	<0.200	<0.020	<0.500	<0.500
9	0.028	47.4	<0.020	<0.020	<0.020	0.044	<0.100	<0.200	<0.020	<0.500	<0.500
11	0.031	48.4	<0.020	<0.020	<0.020	0.042	<0.100	<0.200	<0.020	<0.500	<0.500
13	0.034	48.5	<0.020	<0.020	<0.020	0.043	<0.100	<0.200	<0.020	<0.500	<0.500
15	0.031	43.3	<0.020	<0.020	<0.020	0.043	<0.100	<0.200	<0.020	<0.500	<0.500
17	0.031	43.0	<0.020	<0.020	<0.020	0.045	<0.100	<0.200	<0.020	<0.500	<0.500
19	0.032	43.2	<0.020	<0.020	<0.020	0.046	<0.100	<0.200	<0.020	<0.500	<0.500
22	0.035	43.4	<0.020	<0.020	<0.020	0.039	<0.100	<0.200	<0.020	<0.500	<0.500

Appendix B
Chemical Abbreviations

Chemical Abbreviations

TNT: 2,4,6-trinitrotoluene

RDX: 2,3,5-trinitro-1,3,5-triazine

HMX: oxyhydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

DNB: 1,3-dinitrobenzene

TNB: 1,3,5-trinitrobenzene

4A-DNT: 4-amino-2,6-dinitrotoluene

2A-DNT: 2-amino-4,6-dinitrotoluene

2,6-DNT: 2,6-dinitrotoluene

2,4-DNT: 2,4-dinitrotoluene

3,5-DNA: 3,5-dinitroaniline

2,6-DANT: 2,6-diamino-4-nitrotoluene

2,4-DANT: 2,4-diamino-6-nitrotoluene

AZOXY: composite of 4,2',6,6'-tetranitro-2,4'-azoxytoluene, 2,2',6,6'-tetranitro-4,4'-azoxytoluene, and 4,4',6,6'-tetranitro-2,2'-azoxytoluene

TETRYL: methyl-2,4,6-trinitrophenylnitramine

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13. ABSTRACT *(Maximum 200 words)*

Soil and groundwater contaminated with 2,4,6-trinitrotoluene (TNT) has been identified at a number of military installations. Contaminant transport modeling is an important tool in predicting the fate of this contaminant and evaluating the long-term environmental risk. Modeling efforts require information on the effect of soil heterogeneities on the sorption, desorption, and transformation of TNT.

The objective of this study was to determine transformation and sorption parameters from TNT breakthrough curves (BTCs) under anaerobic conditions for four soils from the Louisiana Army Ammunition Plant. Soil column studies were conducted in thin-disk columns under a nitrogen atmosphere.

Under experimental conditions, sorption and transformation behavior of TNT was limited for all four soils studied. BTCs were fitted with the complete mix model, assuming first-order transformation and linear equilibrium sorption. Distribution coefficients ranged from 1 to 2 ℓ/kg. Transformation coefficients ranged between 0.0080 and 0.0131 hr^{-1}. The principal breakdown products observed were 2A-DNT and 4A-DNT; these were produced in amounts of approximately equal magnitude. In two soils, production of transformation products declined over the period of the study, possibly indicating an exhaustible soil transformation component.

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